



## **CHEMISTRY IN DAILY LIFE**

To V.

# CHEMISTRY IN DAILY LIFE

BY

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WITH 21 DIAGRAMS



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## PREFACE

**I**N the early part of 1928 the author gave at Plymouth, under the auspices of the Education Authority and of the University College of the South-West, Exeter, a course of Extension Lectures on 'Chemistry in Daily Life'. The audiences included a medical practitioner, some business men, school teachers and a number of senior scholars from local schools. During May of this year the B.B.C. broadcast a series of five talks by the author on the same subject, and a number of listeners were interested enough to write and ask for further information. Curiously enough, amongst the letters received one came from a Harley Street doctor and another from a school-girl! The broad appeal of which an account of the achievements of chemistry was capable stimulated the author to write this book, but it is in the attempt to satisfy the requirements of different types of readers that the main difficulty has been encountered. Every effort has been made to simplify the style as much as possible, but in doing so the author hopes that he will not leave the impression that chemical discoveries can be made without a great deal of skilful work as well as brilliant thought.

It is hoped that the book will be of interest to the general reader and be useful as a basis for extension, and similar lectures for adults, as well as a text-book for schools, whether chemistry is taught or not. For students of different types a number of questions and essay subjects of varying degrees of difficulty, and the titles of books suitable for reference have been included at the end of each chapter. To most of these books the author is himself indebted for much useful material.

The author wishes to express his thanks to Professor R. H. A. Plimmer and the Controller of H.M. Stationery Office for permission to use the table on p. 125; to Sir Gowland Hopkins, the Editors of the *Journal of Physiology* and the Cambridge University Press for allowing the reproduction of Fig. 16; to Dr. G. M. Bennett for reading and criticizing the proofs; and particularly to Miss V. F. Collingwood, of St. Hilda's College, Oxford, for valuable help in the preparation of the manuscript for the press and for drawing most of the diagrams.

S. G.

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# CHEMISTRY IN DAILY LIFE

## CHAPTER I

### THE BEGINNINGS AND DEVELOPMENT OF CHEMISTRY

MANY of us have been led by curiosity, at some time or another, to take to pieces a watch or other form of mechanism in order to find out how it is made, and why it works. Many of us have tried—frequently perhaps in vain—to put together the pieces with the hope of obtaining better results than before. We have all been moved by a natural instinct to find out—curiosity we generally call it—and it is this instinct which has produced the vast amount of ordered scientific knowledge of to-day. Chemistry, in particular, is the story of man's attempts to discover what things are made of, his search for the structural units, or simplest bricks—or what we call in scientific language, the elements—from which all material things are built up. This, however, only represents the analytical side of the chemist's work, for chemistry also tells of the efforts which have been made to rebuild the old structures—once the building units have been discovered—as well as of the attempts to prepare new materials with new properties.

The synthetic or 'building-up' aspect of chemistry represents the great development of the last century. As a result of the analysis of a large number of different materials it has been observed that certain groupings of elements are associated with particular properties; thus one particular grouping produces a sweet taste, another grouping may confer a poisonous nature, whilst a third may yield a dyestuff, and so on. Synthetic chemistry has made use of these discoveries and attempted, frequently with astonishing success, to construct substances with certain desirable qualities, but without

other objectionable ones which might exist in a natural material. For example the plant product cocaine is very valuable as a local anesthetic—it temporarily deadens the nerves at the point at which it is injected—but unfortunately it is a poison and must be used only with caution. By studying the groupings of elements in cocaine and in other substances, the chemist has been able to prepare materials which have the desirable anesthetic power of cocaine but not its poisonous nature.

The chemist not only finds out of what things are made; he is also concerned with observing and classifying the changes which occur when various substances react with one another to produce materials with entirely different properties. Such changes as these are called chemical changes, as distinct from the temporary, or physical changes. If a piece of iron is raised to red heat in a fire, the change the metal undergoes is a physical one since on cooling it is restored to its original condition; a careful examination shows, however, that a thin film has formed on the surface. This film consists of oxide of iron, an entirely new material, resulting from the chemical reaction which has occurred between the iron and the oxygen present in the air. Chemical changes are very frequently encountered in everyday life; the production of fire, the rusting of metals, the digestion of food, the growth of plants and the souring of milk are common daily events in which various materials undergo complete or chemical change. To restore the resulting products to their original condition is a matter of great difficulty—almost of impossibility; that is, in fact, one of the characteristics of chemical change.

This aspect of chemistry has enabled us to understand more clearly many of the processes which we meet in our lives, and we have frequently been able to improve them quite considerably. For example it has been known for thousands of years that farmyard refuse was an excellent fertilizer and helped the growth of plants, but it is only comparatively recently that the reason for this has been discovered, and now it is possible to replace or supplement the limited supply of natural manure by others obtained in almost unlimited amount from chemical sources. We know more clearly as a result of chemical study why iron rusts, and so we have been able to devise methods for its protection as well as to invent rustless alloys. The investigation of

explosive reactions is not only helping to improve the internal combustion petrol engine, but it is also throwing light on the causes of deadly explosions in mines, and is suggesting means of preventing them. These are random examples which serve to show some of the applications of chemical changes ; there are, needless to say, very many others.

Chemistry also plays a great part in the industries of to-day. It is true that hundreds, even thousands, of years ago, some people were able to make soap and glass, to extract metals from their ores, to make pigments and to dye fabrics ; these men performed chemical reactions, but in an entirely empirical and rule-of-thumb manner discovered as a result of the process of trial and error. A slight change of circumstances would ruin the results because the reactions were not really understood. Now we can deliberately adjust the physical conditions so as to give the best possible and most desirable results ; further, we can make valuable use of materials which were at one time considered useless or even worse than useless. A striking example of this is the product of the gas works, namely coal-tar (p. 193) ; at one time it was a burden to industry, now it is a valuable source of raw materials. There are very few substances handled by us in our daily lives which are not connected in some way with chemical processes ; many of these processes are comparatively simple, and some of them will be discussed in subsequent chapters of this book, but many are so complex that we are only now, after many years of study, on the fringe of the problems which they present.

The study of chemistry is not only of practical and utilitarian value ; it definitely has also a cultural side. Even a general knowledge of the subject can broaden one's outlook and give a greatly added interest to life ; new possibilities are opened up in the heavens and in the earth. The admiration of a beautifully coloured fabric is not decreased, but should rather be enhanced because we know of the complicated arrangement of atoms which has resulted in the production of this particular colour, or because we are told that the chemist in his laboratory has been able to produce a silk-like fabric without using a silkworm. All knowledge which gives an increased sense of proportion is culture, and in this respect chemistry has definitely something to contribute.

Before proceeding to discuss some of the applications of chemistry in daily life, it will be interesting to review the historical development of the subject with particular reference to the concept of an element. The first ideas concerning the constitution of matter appear to have come from the Far East over 4,000 years ago. Whilst Europe was still over-run by barbarians, the Hindu philosophers and the Chinese Buddhists conceived the universe to be built up from earth, water, fire, wind and aether. It is impossible for us to say exactly what the Oriental thinkers had in their minds, but it is most probable that these five constituent units of the universe were regarded as symbols rather than real entities. Whether these ideas were forgotten or whether they had any influence on subsequent thought it is impossible to tell, but the fact remains that during the 500 years which preceded the Christian era the Greek philosophers, Empedocles, Plato and Aristotle, made suggestions along similar lines. They thought that all things were made up from four elements, namely, earth, air, fire and water; this theory in various forms held its ground for nearly 2,000 years, and the relics of it are still to be found in the word 'elements', used in such a phrase as 'battling with the elements' when referring to the forces of nature.

Even though the Greek philosophers are much nearer to us than the Chinese Buddhist thinkers, yet we are uncertain as to the real interpretation to be put even on the Greek idea of the elements; some people undoubtedly regarded the elements as referring to the material air and water, whilst others considered them to be more in the nature of principles or representations of physical properties. Aristotle, for example, thought that there was only one kind of matter, and this could take up four qualities, hot, cold, dry and moist; when these qualities clothed matter in pairs, the four elements were supposed to result. Thus air was hot and moist; water was cold and moist; fire was hot and dry, whilst earth was cold and dry; hence the difference between one material and another was regarded as due to variations in one or more of the primal qualities, but the fundamental matter was always the same. Aristotle also introduced a vague fifth element which was supposed to pervade everything; he called this 'aether' and we have a similar concept to-day in the all-pervading ether of the physicist. It must

be realized that the Greek philosophers were merely thinkers ; they made observations but did not experiment, and consequently it is difficult for us accurately to interpret in terms of modern science exactly what their ideas were.

After the death of Alexander the Great his vast empire was divided, and Alexandria, the capital of Egypt, under Ptolemy, became a great centre of learning ; the Greek ideas concerning the nature of matter were probably adopted here and became the basis of actual practical work. It seems that it was in Egypt that chemistry was born ; 'chemia', or the black art, as it was then called, became the study of the methods of converting base metals into gold. The exact origin of this idea is uncertain. It may have started with dishonest Egyptian goldsmiths who alloyed gold with a cheap metal and pretended to have converted the latter into gold ; possibly the Egyptian priests who dabbled in magic and mysticism, claimed to have the power of converting base metals into gold in order to impress the credulous people with their wonderful abilities ; or perhaps observations such as the colour change of copper to that of gold or silver, brought about by heating with calamine (a zinc ore) or with arsenic, respectively, may have suggested to some earnest seekers after knowledge that a complete transmutation was possible. But although we are uncertain as to who started the search for what was later called the Philosopher's Stone, which was said to possess this wonderful power of transforming base metals into precious ones, yet we know that many people thought the search worth continuing.

Although no progress was made along the direct line of their search, there was very little made even along the many important side-lines of chemistry until the capture of Alexandria by the Arabs in the seventh century A.D. brought new life into the study of the subject now called *al-chemia* <sup>1</sup> (alchemy). The most famous of the Arabic alchemists was Jabir, who lived in Baghdad in the eighth century ; he considered that the search for gold was only one aspect of alchemy and as a result he made many useful discoveries in general chemistry. Jabir is given the honour of discovering oil of vitriol (sulphuric acid), aqua fortis (nitric acid) and aqua regia, which can dissolve gold ; he raised alchemy to the level of an experimental science, and it became a dignified

<sup>1</sup> Al — the (in Arabic).



subject of study. Jabir apparently accepted the four-element theory of the Greeks, but in an extended form; he thought that all metals were made up of a fusible part which he represented by mercury, and a combustible part represented by sulphur. Here again we are uncertain of the exact meaning of 'sulphur' and 'mercury'; Jabir may have meant the actual material substances, but it is more probable that he referred to them as symbols or types.

After the eighth century the study of alchemy spread and apparently reached England in the twelfth century, after Robert of Chester had translated in 1144 an Arabic book on alchemy into Latin. One of the most famous of the English alchemists was Roger Bacon, a monk, who was born in Somerset in 1214; he appears to have had a clear scientific brain and a keen intelligence, but in spite of these qualities he firmly believed in the possibility of the Philosopher's Stone which would convert one million times its own weight of base metal into gold. Roger Bacon is often said to have discovered gunpowder, but it is very probable that this substance was known long before his time. The first known description of the composition of this explosive mixture apparently is to be found in Roger Bacon's writings, curiously enough hidden away in an anagram. In due course seekers for the Philosopher's Stone increased in number, and after the capture of Constantinople—a great centre of learning—by the Turks in 1453, the dispersed scholars spread all over Europe and introduced alchemy as a regular subject of study. By the fifteenth century alchemy had reached its greatest heights, and then began the decline which was, however, to usher in developments of importance destined to lead up to the chemistry of to-day.

In the year 1493 there was born in Switzerland a man of remarkable, although not altogether pleasant, personality generally known as Paracelsus; he studied both alchemy and medicine, and as a result saw the possibilities which marked the opening of a new era. Paracelsus broke completely away from tradition; he said definitely that the object of alchemy was to prepare medicines and not to seek for gold. Thus began the age of Iatro-Chemistry, or medical chemistry, in which the main object of the chemists—the prefix 'al' was dropped—was to prepare and purify drugs and test their efficacy. This new objective had at least one

far-reaching result ; it helped gradually to remove the terrible obsession of the Philosopher's Stone which had gripped the imaginations of all types of people for over 1,500 years.

Some of the alchemists had been actuated by motives of greed or desire to become rich quickly, others by motives of pure scientific interest, whilst others imagined that by making gold commonplace they would actually eliminate the social and political evils for which they thought it to be responsible—but whatever their motives no one was successful in the search. Although the so-called Philosopher's Stone was not actually discovered it must not be imagined that the search proved entirely fruitless ; in the course of their random mixings, heatings and distillations the alchemists obtained perchance penetrating fumes, sometimes with an unpleasant odour, sometimes an explosion or a fire might occur, or a coloured substance would result. Probably in this way there originated a number of useful materials such as vitriol and other acids, phosphorus which played a part in the development of matches, and even possibly picric acid which was first used as a yellow dye and is now, or rather was recently, an important high explosive. Incidentally a large number of observations of chemical changes were made and a knowledge of these proved very useful in the further developments of the science along the new lines which it took mainly as the result of the break from the older ideas made by Paracelsus.

Although the school of iatro-chemistry was not a great success, it had the supreme achievement to its credit of setting the mind of man free from the chains of alchemy, and during the course of the sixteenth and the seventeenth centuries, many interesting lines of investigation were followed up by men who were anxious simply to increase the world's store of useful knowledge. Pre-eminent amongst these was Robert Boyle who was born in Ireland in 1627. Boyle's most important contribution to chemistry was probably his rigid insistence on the principles upon which modern science has been based ; his method was to make experiments, then if possible invent a hypothesis or theory from the results, and finally to devise further experiments to test the theory. The application of these principles helped to raise chemistry from the level of mysticism and empiricism to that of an exact science.

Boyle's other great work was his development of the

concept of an element. In the seventeenth century the Greek idea of four elements was still the accepted basis for views on the structure of matter and upon it had been grafted a vague theory of three 'principles' represented by mercury, sulphur and salt; in his important book entitled *The Sceptical Chymist*, published in 1661, Boyle condemned these ideas in a very severe and outspoken manner. The possibility of transmuting base metals into gold had been founded to some extent on the theories which were generally accepted regarding the constitution of matter, and when Boyle rejected these views he dealt a blow at those who still, in spite of the work of Paracelsus, searched for the Philosopher's Stone. In the same book Robert Boyle introduced, possibly in a rather vague way, our modern idea of an element as something which we are quite unable to split up into simpler constituents; they are the unit bricks from which all substances are built up. Boyle says: 'I mean by elements . . . certain primitive or perfectly unmingled bodies, which not being made of any other bodies or of one another, are the ingredients . . . of mixt bodies. I must not look on any body as a true . . . element which . . . is further resolvable into any number of distinct substances.' Lead and gold are examples of these primitive bodies, or elements; each contains nothing simpler and hence the transmutation of one into the other appears to be a matter of superhuman difficulty. Boyle is sometimes called the 'Father of Chemistry', and there is no doubt that his profound influence on scientific thought marks him out as the founder of a new epoch.

In spite of the work of Boyle, the four-element theory was still generally accepted for at least another hundred years until it was definitely shattered by the work of the brilliant French chemist, Lavoisier—the 'Father of Modern Chemistry'. In 1774 he proved that air was not a simple elementary substance, but a mixture at least of two different gases which we now call oxygen and nitrogen. It had been known for some time that when various substances, such as sulphur or a candle, are burnt in an enclosed quantity of air, only part of the air is used up before the burning ceases; it was at one time thought that this was because the air became saturated with something present in the fire which prevented further burning. In the course of a brilliant series of experiments concerning the nature of combustion, or burning, Lavoisier

had suspected that the air consisted of an active part which was used up, and an inactive part which was always left behind when burning was completed. He had not succeeded, however, in isolating this active portion.

In the meantime Joseph Priestley, a nonconformist clergyman who spent much of his time making random chemical experiments, had made some interesting and important discoveries. He had procured a large burning glass—12 inches in diameter—and with this he proceeded to heat, by concentrating the rays of the sun on them, various substances placed in a glass cylinder over mercury out of contact with the air. On August 1st, 1774—a red-letter day in the history of chemistry—Priestley heated in this way a substance then known as ‘mercurius calcinatus per se’ or the ‘red calx of mercury’, and now called mercuric oxide; he observed that a gas was expelled from it very readily. On examining this gas Priestley was astonished to find that a candle would burn in it with a remarkably brilliant flame, and also that a mouse was able to live in the gas about twice as long as it could have lived in an equal volume of ordinary air. Priestley says that he had the curiosity to breathe the gas himself, and he fancied that his ‘breast felt peculiarly light and easy for some time afterwards’. Unfortunately, Priestley was a great supporter of an erroneous theory of combustion, to which reference will be made later, and hence he was unable to interpret his observations in a satisfactory manner.

Lavoisier, however, was not slow to realize their importance, and he was able to prove that the gas obtained by heating red calx of mercury was the active constituent of the air which was used up in burning and breathing. This active constituent is now called oxygen and on mixing it with the inactive residue which remains after burning has ceased—now called nitrogen—the original air is regenerated. Naturally in the pure oxygen, obtained by Priestley, burning and breathing would take place much more actively than in air which contains a large proportion of an inactive diluent. In this way the Greek idea of the elementary or simple nature of air was disproved; it could no longer, of course, be considered as an element if it could be divided up into two parts with such entirely different properties. Lavoisier’s work marked the ‘beginning of the end’ for the four-element theory, and the modern view of an element, as originally outlined by Boyle,

began to be more generally adopted. In 1789 Lavoisier said : ' We apply the term elements . . . to bodies to express our idea of the last point which analysis is capable of reaching '. An element is, therefore, a substance which contains, as far as we know, only one kind of matter, and we are unable to split it up at will into simpler forms of matter. On this basis Lavoisier described about twenty different substances as elements—instead of the four previously imagined to exist ; amongst these, however, were materials like lime and magnesia which have subsequently been proved to be made up of two different elements.

During the past 140 years many claims have been made to the discovery of new elements which had not been previously recognized ; some of these claims were erroneous but many were confirmed, and at the present time ninety different elements are known to exist on the earth. All known substances are made up from one or more of these elements, which may be united together in many different ways. Scientists have been able to arrange the known elements in order of increasing weight as a result of measurements made with X-rays (p. 30) ; when this is done there are found to be two gaps corresponding to two elements which have not yet been identified. We have the possibility to-day, therefore, of ninety-two different elements on our planet ; of these the gas hydrogen is the first and simplest, and uranium is the ninety-second and most massive element.

Thus the work of the chemists in one direction at least—the search for the structural units from which all substances are built up—is almost complete. But there is still much more to be done in other ways. When two or more elements unite together chemically, there is a firm connexion between them which results in the production of an entirely new substance separable into its constituents only with difficulty ; we then say that chemical combination has occurred and a chemical compound is formed. There are probably over a quarter of a million different compounds known and the chemist has set himself the task of finding out exactly how the elements are built up into these compounds. Starch, sugar, alcohol, glycerine, acetic acid (vinegar), carbolic acid and aspirin, to name a few common substances, are all made up of the three elements carbon, hydrogen and oxygen, yet they all have entirely different properties ; the chemist has sought

and found the explanation—it is a question of the arrangement of the elements. The first step towards the solution of this problem was made by John Dalton at the beginning of the last century and his work will be discussed in the next chapter.

#### QUESTIONS

1. Enumerate examples of chemical phenomena in daily life.
2. What is meant by a chemical change?
3. How did the idea of the Philosopher's Stone develop?
4. Distinguish between an element and a compound.

#### SUBJECTS FOR ESSAYS AND DISCUSSION

1. The development of the concept of an element during the past two thousand years.
2. The possible consequences of the discovery of the Philosopher's Stone.
3. Chemistry as part of a general cultural education.
4. The stages in the history of chemistry.

#### FURTHER STUDY

1. The contributions to science of Paracelsus, Boyle, Priestley, Lavoisier and Scheele.
2. The chemical knowledge and discoveries of the Arabs.
3. The history of the discovery of the chemical elements.
4. The influence of progress in general learning on contemporary developments in chemistry.

#### BOOKS TO READ

Alchemy: Its Science and Romance. Mercer. (S.P.C.K.)  
Chemistry to the Time of Dalton. Holmyard. (Oxford Univ. Press.)  
Three Centuries of Chemistry. Masson. (Benn.)  
Famous Chemists. Tilden. (Routledge.)  
A History of Chemistry. Brown. (Churchill.)  
Chemistry in Modern Life. Arrhenius. (Chapman and Hall.)  
A Concise History of Chemistry. Hilditch. (Methuen.)

#### SUGGESTIONS FOR EXPERIMENTS

Replacement of copper by zinc and iron.  
Preparation and heating of mercuric oxide.  
Burning substances in a limited supply of air.  
Heating iron and sulphur.

## CHAPTER II

### THE STRUCTURE OF MATTER

**M**OST of the ninety known elements are only found to a very small extent in nature; in fact, 99 per cent. of those parts of the earth which can be examined, namely the atmosphere, the ocean and the solid crust of the earth to a depth of about 10 miles, have been found to consist of only twelve elements. Thus the other eighty possible elements are comparatively rare—some more so than others—as altogether they only make up one-hundredth part of the known portions of the earth. The following table gives the percentage of the twelve most common elements as calculated by the American, F. W. Clarke :

Oxygen . . .	50.02	Calcium . . .	3.22	Hydrogen . . .	0.95
Silicon . . .	25.80	Sodium . . .	2.36	Titanium . . .	0.43
Aluminium . .	7.30	Potassium . .	2.28	Chlorine . . .	0.20
Iron . . . . .	4.18	Magnesium . .	2.08	Carbon . . . .	0.18

Thus oxygen which constitutes about one-fifth part of the air and eight-ninths of water, is the most common of all elements; in combination with silicon, the next common element, it forms silicon dioxide, or silica. This is the chief constituent of sand and quartz, and it also occurs, in a combined form, in a large number of rocks and minerals. The most common metal is not iron, as one might have imagined, but aluminium which is found in many mineral substances, particularly in felspar (from granite) and in clay. It is very probable, however, that the centre of the earth consists mainly of iron. The average density of the earth's crust, surface and atmosphere has been calculated to be about 2.7, whereas the mean density of the whole earth is about 5.4; this means that the centre of the earth must consist mainly of heavy metals having a density between 7 and 8. Iron has a density of 7.9, and in view of the fact that iron is known to occur to a great extent in the sun and that it is an

## THE STRUCTURE OF MATTER

important constituent of meteorites which were once part of another planet or star, it seems very probable that it is an important constituent of the earth below the crust.

The chief elements found in living things are carbon, hydrogen, oxygen and nitrogen, but there are also present very small amounts of calcium, magnesium, iron, phosphorus, potassium, sodium, chlorine and iodine. All common metals such as copper, zinc, iron, tin, silver, gold and mercury are known to be elementary in their constitution. Brass and

bronze, however, are not elements. It is quite common and often convenient to divide up all the elements into the categories of metals and non-metals; metals generally have a characteristic lustre; they can usually be hammered out into thin sheets and drawn into wires, and they conduct heat and the electric current. Non-metals are the other elements which have not these physical properties. There are also chemical properties which enable us to distinguish between

metals and non-metals. When a non-metal—for example, sulphur, carbon or phosphorus—burns in air it combines with the oxygen to form an oxide; if this oxide is added to water the solution is found to have a sour taste and to possess corrosive properties—the solution is said to contain an ‘acid’. It is general to test for the presence of an acid by means of certain coloured substances called indicators; one of the most common of these is a dye called litmus, extracted from certain lichens, the blue colour of which can be turned red by an acid. A similar colour change is observed during the pickling

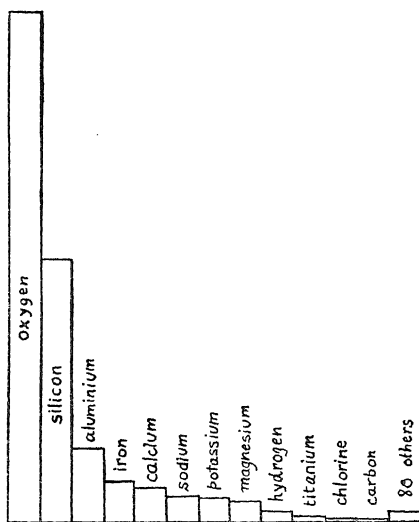


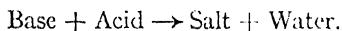
FIG. 1.—Distribution of the Elements in the Earth's 'Crust'



of cabbage ; the original purple of the cabbage is turned red by the acid present in vinegar. By applying this simple test, as well as more complicated ones, it is found that in general the compound of a non-metallic element with oxygen, usually the result of burning, forms an acid in solution ; we call these compounds acidic oxides.

It is as well to mention that there are many acids other than those obtained in this way, but they all have the same characteristic properties ; several of these acids are found in nature. Thus citric acid is the cause of the sourness of the lemon, and it can be extracted from lemon and lime juice in a crystalline form ; the acid is also found in other fruits before they are ripe. Sour apples contain malic acid, and grapes tartaric acid ; fermented alcoholic juice can yield vinegar which contains acetic acid, whilst sour milk contains lactic acid. The most common acids are the so-called mineral acids which are very important in chemical industry ; they are : sulphuric acid (oil of vitriol), nitric acid (aqua fortis) and hydrochloric acid (spirit of salt). These are all extremely corrosive substances and must be handled with care.

The oxides of metallic elements are called 'bases' and they have properties which are exactly opposite to those of the acidic oxides. A base is able to neutralize or remove the acidic properties from an acid ; the substance which results from the interaction of these two is in general no longer sour nor does it turn litmus solution red. This resulting substance is called a 'salt' and we can describe the neutralization reaction in the form of the relation :



The name given to the salt is a combination of that of the metal present in the base and of the acid. Thus when copper oxide neutralizes sulphuric acid, we get a salt called copper sulphate (blue vitriol) ; the neutralization of hydrochloric acid by the oxide of sodium would give sodium chloride, which is in fact identical with common, or table salt. There are many hundreds of different salts known since there are over sixty metals, as well as many other groups of elements which in this respect behave like metals, and most of these can form salts with each of the large number of different acids ; the substance which we are in the habit of calling 'salt', or 'common salt', is merely one of many possible salts. A

considerable number of salts are found in nature besides common salt ; thus the sea contains in addition magnesium chloride and a number of salts of the metal potassium. Limestone, marble and chalk are all three chemically identical and consist of calcium carbonate, which is the calcium salt of carbonic acid (p. 77). Chile saltpetre, vast deposits of which exist in South America, is a salt of nitric acid known as sodium nitrate, whilst bone ash contains mainly calcium phosphate, a salt of phosphoric acid.

When a basic oxide, or base, is soluble in water the solution generally has a burning or caustic taste, is slippery to the touch and has the power of restoring the blue colour of litmus which has been reddened by acid ; such solutions are said to be alkaline ; the basic oxide, or its compound with water, is called an ' alkali '. Alkalies such as caustic soda, or sodium hydroxide as it is referred to by the chemist, are used in the manufacture of soap ; burnt lime is also an alkali which is used for making lime water.

We have now given a brief explanation of some common terms used in chemistry and it is hoped that the reader has grasped their meaning to a sufficient extent to understand any reference made to them in subsequent pages.

A new phase in the development of chemistry as an exact or quantitative science was made by John Dalton in the early years of the eighteenth century. Dalton was born in Cumberland in 1766, the son of poor parents ; after various attempts at earning a living he went, in 1793, to Manchester, where he gave lessons in mathematics and devoted his leisure to the study of chemistry. It was in that city that he first formulated one of the most important of chemical theories—now known as Dalton's Atomic Theory—an account of which was first published in 1807. Dalton in his theory revived in a more definite and practical form an idea which had been suggested over 2,000 years previously by the Greek philosopher Democritus and which had been described in a realistic manner by the Roman poet Lucretius in his *De rerum Natura*. This idea was that all material things were made up ultimately of small indivisible particles called ' atoms '.

If we take a piece of iron, say, and break it up into pieces and each piece into smaller pieces and so on until a point is reached at which the particles of iron are so small that they cannot be further subdivided—at least without ceasing to be

iron—then these smallest particles are the atoms of iron. We know now that these atoms are so small that they cannot be rendered visible even by the most powerful microscopes in existence, or ever likely to exist! Originally the atoms of different substances, in agreement with the ideas of Aristotle (p. 4), were all supposed to be made of the same primitive matter, but it was thought that they might have different sizes and shapes, and vary in roughness of surface. Dalton, however, had a much clearer idea; he considered that all the atoms of any particular element were exactly alike in appearance, weight, size and other properties, but they differed entirely in their nature from the atoms of any other element. According to Dalton, elements form compounds as a result of the union of a definite whole number of atoms of one kind with a definite whole number of another kind. The composition of the compound will depend on the number and nature of the atoms which it contains, and since these are perfectly definite the composition of the compound must also be definite. This is the most fundamental law of chemistry because it tells us that when we are dealing with a particular compound it does not matter how, where or when it was made, provided the substance is pure it will always have exactly the same composition. For example, if we start with one gram of pure copper it can be converted into copper oxide in a number of different ways, but in every case we obtain only 1.252 grams of oxide compounded of 1 gram of copper and 0.252 grams of oxygen. Without this constancy of composition, chemistry could not possibly have been an exact science. Dalton went a stage further and considered the possibility of two elements, which we may call A and B, combining together to form more than one compound; in each case a small but whole number of atoms of A would combine with a small but whole number of atoms of B and such compounds as  $(A + B)$ ,  $(A + 2B)$  and  $(2A + B)$ , etc., might result. Each of these would be a definite substance, but each would be different from the others.

One of the tasks which Dalton set himself, was to compare the weights of the different atoms with one another; he took hydrogen—the lightest atom—as having a weight of unity, and the corresponding weights of other atoms were called their ‘atomic weights’. Unfortunately the atoms are so small that they cannot be weighed directly, and atomic weights are

## THE STRUCTURE OF MATTER

determined by a number of devious methods too technical to explain here. Dalton had very little information to work on and hence he made certain erroneous assumptions with the result that many of his atomic weights were incorrect ; in recent years, however, increased chemical knowledge has enabled us to determine atomic weights with great accuracy. Some examples of these atomic weights of common elements are given in the table below—on the assumption that the weight of an atom of hydrogen is 1.0077, instead of 1.0. We shall see later that these values, some of which are whole numbers, are of great interest.

ATOMIC WEIGHTS					
Helium (He)	4.00	Phosphorus (P)	31.04	Copper (Cu)	63.57
Carbon (C)	12.00	Sulphur (S)	32.06	Zinc (Z)	65.37
Nitrogen (N)	14.01	Chlorine (Cl)	35.46	Tin (Sn)	118.7
Oxygen (O)	16.00	Potassium (K)	39.10	Gold (Au)	197.2
Sodium (Na)	23.00	Calcium (Ca)	40.07	Lead (Pb)	207.2
Silicon (Si)	28.3	Iron (Fe)	55.84	Uranium (U)	238.2

When the elements are arranged in general in order of increasing atomic weight, allowance being made for the two missing elements, then the position of any particular element in this series is called its 'atomic number'. Thus the atomic number of hydrogen, the lightest atom, is 1, for helium it is 2, for oxygen 8, for chlorine 17, and for uranium, the heaviest atom, 92. It will be shown subsequently that the atomic number has an important connexion with the internal structure of the atom itself.

An examination of the chemical and physical properties of the elements when they are arranged in order of the increasing weights of their atoms, has brought out an interesting regularity ; if we ignore hydrogen, then the first eight elements are almost paralleled by the second eight. After this comes a group of eighteen elements followed again by a somewhat similar group of eighteen ; the first few and the last few elements of these groups of eighteen bear distinct resemblances to corresponding elements in the two groups of eight. The fifth group, or period as it is generally called, contains thirty-two elements and includes a set of eighteen which resemble those of the previous period. The last and sixth period is incomplete as only six of its elements are known. The regular repetition of properties observed in passing from one group to another, and the gradations found within each group or period have been very helpful in indicating the properties as

well as the sources of unknown, or little known, elements.

In the above table of atomic weights, it will be observed that certain letters have been placed in brackets against the name of each element; these letters represent the symbols used by chemists for representing the elements. Thus instead of writing the phrase 'one atom of chlorine', we simply write 'Cl' and that conveys exactly the same meaning. The system of symbols is a kind of chemical shorthand; it has been in use, in different forms, for very many years, but our present system is only about a hundred years old. As a rule, the symbols are obtained from the initial letter or letters of the name of the element; sometimes the Latin name has been made use of, as, for example, in the case of sodium, the name for which in Latin is 'natrium'. The symbols are also used to represent the formula of a compound; thus copper oxide is written 'CuO'. This tells us that one atom of copper and one atom of oxygen have combined together chemically. Water is written  $\text{H}_2\text{O}$  because here two atoms of hydrogen have entered into combination with one atom of oxygen. A complex formula is  $\text{H}_2\text{SO}_4$ , that for sulphuric acid, since this acid is a compound containing two atoms of hydrogen, one of sulphur and four of oxygen. In general we can represent the composition of any compound by means of its formula, and this is a great convenience to chemists, especially when describing a chemical reaction.

Dalton in his theory did not distinguish between the smallest part of an element and that of a compound; he called them both atoms—'elementary atoms' and 'compound atoms' respectively. This caused some difficulty, however, which was overcome by the modification made by an Italian chemist named Avogadro, in 1811; he suggested that the term atom should be used only for the smallest part of an element which can take part in a chemical combination or in an exchange with other elements, whilst the smallest portion of any substance, element or compound, which can exist in a free state he called a molecule. We are thus able to speak of an atom or molecule of an element, but only of a molecule of a compound; if the latter is broken up it produces the atoms of its constituents. The weight of a molecule of any compound when compared with the weight of an atom of hydrogen as unity (or more generally 1.0077) is called the molecular weight; it is determined by indirect methods.

The chemist believes that all matter is made up of myriads of molecules and that these molecules are perpetually vibrating or else moving about from place to place. This idea seems rather absurd when applied to such a solid body as a bar of iron or a table, but even in these cases we have reason to believe that the vibrating molecules are present. In a solid the molecules are so close together that they attract one another strongly, and so they are able to cling together by what is called 'cohesion'. When a solid is heated, the molecular movement is increased; as a result of more vigorous vibration the molecules are driven further apart and so the cohesion is decreased. At a certain temperature, therefore, the force of cohesion is reduced to such an extent that the molecules can separate and the substance no longer has a fixed shape, but can flow from one vessel to another; in other words the solid has been turned into a liquid and we say that the solid has melted. In the reverse way, if we cool a liquid, we can reduce the extent of the molecular movement until the force of cohesion is sufficient to produce a solid; in this way we can freeze a liquid. Thus the change from ice to water, and vice versa, is due to a change in the motion of the water molecules brought about by a decrease of temperature. If liquid water is heated further we know that it will boil and produce a gas or vapour called steam; this change from liquid to gas will always occur as a result of heating, unless the liquid decomposes before its boiling-point is reached. Again the effect of heat is to make the molecules more energetic in their movements with the result that they are now driven considerable distances from one another; a gas is, in fact, a comparatively empty space, and if we could magnify a small volume of gas about one hundred million times, it would look like a few gnats flying in a space as big as a cathedral! This explains why a gas is so intangible and cannot be placed in a vessel unless the latter is closed up completely; there is no cohesion to keep the molecules from spreading or diffusing.

The actual velocity of a molecule of gas will depend on the nature of the gas and upon its temperature; the lighter the gas and the higher its temperature the more rapidly do the molecules move. At ordinary temperatures the hydrogen molecule—the lightest and fastest—will move at an average rate of a little over a mile per second! When a substance is heated, the heat which is a form of energy is converted

into the energy of motion, or kinetic energy, and the speed of the molecules is increased; the speed of a molecule is, in fact, a measure of its temperature. In some of the hot stars it has been estimated that a temperature as high as 20,000,000° Centigrade exists; this means nothing to us at all considered purely as a temperature, but from another point of view it simply means that the speed of the molecule has been increased to the rate of several thousand miles per second—nothing out of the ordinary when dealing with molecules!

Although the existence of air had been realized for many years—probably as a result of wind which is due to the movement of air—yet owing to the intangibility of gases it was not known until the beginning of the seventeenth century that there could be gases other than air. The term 'gas' was first introduced by Van Helmont, who was born in Brussels in 1577; he found that a non-inflammable gas was obtained when sweet liquors were fermented, whilst in other ways an inflammable gas could be obtained. Although Van Helmont only knew of two gases, we now know a large number which differ from one another in many ways. In fact, any substance on heating will generally yield a gas. Common gases in daily life are oxygen and nitrogen, which are the chief constituents of air, hydrogen which is used for filling balloons and airships, carbon dioxide which results from breathing, burning and fermentation, and is used for making soda-water, sulphuretted-hydrogen to which the smell of a bad egg is partly due, and of course, steam. On cooling a gas we can generally convert it into a liquid; this is the process known as condensation or liquefaction, and takes place at a normal temperature in the case of steam. But when we try to liquefy a gas like air, the problem is far more difficult because a very low temperature must be obtained, as well as a high pressure which has the effect of forcing the molecules close together. By bringing the temperature down to about  $-150^{\circ}\text{C}$ ., or  $-240^{\circ}\text{F}$ ., and increasing the pressure to about 35 atmospheres, that is over 500 pounds to the square inch, it is possible to cause ordinary air to become a liquid; if the temperature is allowed to increase or the pressure to decrease, then the liquid will turn into a gas once more. If liquid air is allowed to evaporate gradually the constituent with the lower boiling-point, which happens to be nitrogen, will evaporate off first and the residual

liquid will be richer in oxygen ; this is the basis of an important method for obtaining almost pure oxygen from air. Hydrogen and helium are the most difficult gases of all to liquefy ; in the latter case a temperature of at least  $-268^{\circ}$  C. has to be attained, and this fact has made the separation of helium from other gases a commercial possibility. On further cooling a liquid, a solid can be obtained, and even solid hydrogen and helium have been produced in this way. The difference between solid, liquid and gaseous 'states of matter' as we usually call them, is thus merely a question of the motion of the constituent molecules, and their power of cohesion, both of which depend mainly on the temperature.

In daily life one frequently meets people who use the word 'melt' in an incorrect sense ; for example, they often say 'the sugar melts in the tea'. It is correct to say that ice melts, but the sugar *dissolves*. Salt, sugar, washing soda and a large number of other substances are soluble in water and they form solutions ; the water in this case is said to be a solvent or dissolving agent. On boiling the water right away, the dissolved substance will remain behind ; this observation led to the belief held at one time that water could be turned into earth because a solid residue was frequently left after long boiling. It was, of course, simply the dissolved matter separating out. Water is one of the best-known solvents, but it is not by any means a solvent for everything. It does not approach by a long way the 'Alkahest', a universal solvent for which some of the older alchemists were searching. Such substances as sand, limestone, carbon and most metals are almost completely insoluble in water, and so also are many compounds of carbon which are of great technical importance. For various purposes other solvents are frequently used in industry ; alcohol is used as a solvent in the preparation of tinctures for medicinal purposes, acetone is used in the manufacture of cordite, whilst naphtha is used as a solvent for grease in dry-cleaning processes. In the last few years the growing use of nitrocellulose lacquers which can be applied, for example to the coach-work of a motor-car, by means of a spray, has necessitated the production of a number of entirely new commercial solvents which until recently were regarded merely as chemical curiosities. The manufacture of these solvents represents one of the great achievements of modern chemical industry.



When a solid dissolves in a liquid it is considered that the former is completely broken up into its molecules, and that these are distributed evenly throughout the whole of the liquid. The particles of dissolved solid are so small that they cannot be seen with the most powerful microscope in existence, and further, they can pass through porous blotting paper, or through filter paper which contains even finer pores. If we add sand or soot to water they do not dissolve, but on shaking up we may get a suspension from which the solid may be readily removed by filtering through porous paper. In between the true solution, in which the dissolved particles are molecular in size, and the suspension, in which the particles are comparatively large, there exists a class of liquids known as *colloidal* solutions which play an important part in life processes. In these systems the suspended particles are too small to be separated by a filter, yet they are much larger than molecules and so can be made visible by using a powerful microscope with a special attachment. Observation in this way has shown that the particles in a colloidal solution are in a continual state of violent motion; they dart and dash about ceaselessly in all directions, presumably for ever. This phenomenon is known as the Brownian movement, since it was discovered by a botanist named Brown in 1827, when examining some pollen grains under the microscope; we now believe that the movement is due to the bombardment of the suspended particles by myriads of small molecules which make up the liquid medium. What we see is not the actual movement of the molecules, but rather a magnified picture of it.

Using this idea as a basis, the French scientist Perrin and others have been able to calculate the size and weight of a molecule, as well as the number in a given volume of gas or liquid. The magnitudes determined are so much out of the general order of measurements that it is impossible to conceive their significance without the aid of analogies. Let us imagine for example, that we had some means of magnifying a tennis ball to the size of the earth; a molecule of water, under these conditions, would be about the size of a small pea! About 100 million molecules of oxygen, say, would have to be laid side by side in order to make a row an inch long; whilst if all the molecules in a cubic inch of air were placed alongside one another, we should have a line which could extend about

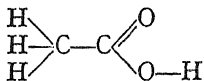
1,400 times round the earth ! The actual weight of a molecule of any substance is obtained by multiplying the actual weight of an atom of hydrogen by the 'molecular weight' of the substance ; the hydrogen atoms are so light that a billion-billions of them would only weigh about a twentieth part of an ounce ! The smallest speck that can be seen in a microscope is just over a hundred-thousandth of an inch in diameter, and even this may contain a million or more separate molecules ! These figures give a faint idea of the minuteness of the atom and the molecule, and make one realize the vast numbers that have to go to make up something that is visible and tangible. Various methods of experiment and observation have all yielded similar results, and so scientists feel fairly confident that their fundamental theory of the molecular constitution of matter is a correct one.

Although molecules are the smallest portions of matter which can exist, yet every molecule must be built up from a number of similar or different atoms. In the case of the molecule of an element all the atoms must naturally be similar, but the number varies with different elements. In the case of some gases, such as the inert gases of the atmosphere to which we shall have occasion to refer later, and the vapours of some metals, the molecule and the atom happen to be identical ; hydrogen, oxygen, nitrogen and chlorine on the other hand, are elements in which two atoms go to make a molecule, whilst phosphorus and sulphur require four and eight atoms respectively. In a compound there must be at least two different kinds of atoms and the properties of the compound depend on the nature, number and arrangement of these atoms. Thus a molecule of water contains two atoms of hydrogen and one atom of oxygen, and so the formula for the molecule, as we have seen, is  $\text{H}_2\text{O}$ . Some molecules are much more complex and contain a large number of atoms ; thus a molecule of cane sugar contains twelve atoms of carbon, twenty-two of hydrogen and eleven of oxygen, and so we write the formula  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ . A molecule of starch, rubber, chlorophyll or albumen may contain thousands of atoms of not more than four or five kinds.

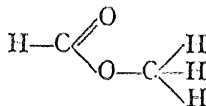
The simple formula which tells us the number of each kind of atom in the molecule does not, however, give us a complete picture. For example the formula  $\text{C}_2\text{H}_4\text{O}_2$  is applicable either to acetic acid, a sour corrosive liquid with a pungent

## CHEMISTRY IN DAILY LIFE

odour and the important constituent of vinegar, or else to methyl formate, which has a pleasant fruity smell. This marked difference in properties is due to the difference in the arrangement of the eight available atoms: the chemist has discovered that these atoms are built up in the two ways represented by the diagrams below.



acetic acid



methyl formate

These diagrams are called 'structural formulæ' because they show how the molecule is built up or constructed from its constituent atoms. Each letter represents an atom and a line joining two atoms is meant to represent a chemical bond of union, or as it is generally called, a 'valency bond', between the two atoms. It will be observed that a carbon atom always has four valency bonds, oxygen two and hydrogen one. Thus carbon, oxygen and hydrogen are said to have valencies of four, two and one respectively, and these values hold good in the vast majority of compounds which contain any or all of these elements. Valency, therefore, appears to be a fundamental property of the atom. Every element has a more or less definite valency which gives us an indication of exactly how many atoms of other elements can combine with one atom of the particular element. Valencies are invaluable in helping us to build up structural formulæ and to learn what groupings are present in different compounds; similar groupings very often mean similar

properties. Thus the group  $-\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OH} \end{array}$ , which is present in

acetic acid (see above) is found to confer acidic properties upon any compound in which it happens to be present; the

grouping  $-\text{N} \begin{array}{l} \diagup \text{H} \\ \diagdown \text{H} \end{array}$  confers, on the other hand, basic properties.

The group  $-\text{O}-\text{H}$  under certain conditions gives a series of compounds called the 'alcohols'; of these substances methyl alcohol (wood spirit) and ethyl alcohol (ordinary alcohol) are well-known instances. In general every grouping is

associated with distinctive qualities and each has the power of conferring some definite property on the compound in which it is present. On the whole the study of structural formulæ has been extremely fruitful, especially in connexion with the chemistry of carbon compounds. Not only have chemists been able to build up compounds with particular properties, but also by knowing what arrangement of atoms is present in any special compound, they have known with what raw materials to start in order to build up, or synthesize, it.

## QUESTIONS

1. How do metals and non-metals differ in their physical properties?
2. Describe the differences in properties of the oxides of metallic and non-metallic elements.
3. What is a salt? Name some salts frequently used in daily life.
4. What is the difference between an atom and a molecule?

## SUBJECTS FOR ESSAYS AND DISCUSSION

1. The properties of common metallic and non-metallic elements.
2. The value of symbols and formulæ in chemistry.
3. Dalton's part in the progress of chemistry.
4. The molecular theory of matter.

## FURTHER STUDY

1. The determination and application of atomic and molecular weights.
2. The liquefaction of gases.
3. The classification of the elements.
4. The kinetic theory.

## BOOKS TO READ

The Study of Chemical Composition. Freund. (Camb. Univ. Press.)  
Foundations of Chemical Theory. Caven. (Blackie.)  
Matter and Energy. Soddy. (Home Univ. Library.)  
Everyman's Chemistry. Hendrick. (Univ. of London Press.)  
Chemical Discovery and Invention in the Twentieth Century. Tilden. (Routledge.)  
The Liquefaction of Gases. Hardin. (Macmillan.)  
Outlines of Physical Chemistry. Senter. (Methuen.)  
The Structure and Properties of Matter. Caspari. (Benn.)

## SUGGESTIONS FOR EXPERIMENTS

The action of various solutions on litmus.  
The colour changes of red cabbage.  
The preparation of simple salts.  
The preparation and properties of various elements and oxides.

## CHAPTER III<sup>1</sup>

### ELECTRICITY AND THE ATOM

WE have in the previous chapter obtained some idea as to how the atoms are built up into molecules, and we naturally inquire further: 'Of what is an atom made?' When we think of the extreme minuteness of the atom, which we can never hope to see even through a microscope, it seems a hopeless task to inquire into its structure. Until thirty years ago it appeared impossible even to conjecture on this subject, but an accumulation of observations, made particularly in the fields of electricity and radio-activity, has thrown some light on a difficult but fascinating problem. In order to be in a position to follow the conclusions arrived at it is essential to have some knowledge of electricity, and so it will be necessary to digress for a short while in order to convey to the reader the rudiments of this subject.

If some dry glass is rubbed with a dry piece of silk the former acquires the property of picking up light objects such as small pieces of paper or feathers; a piece of sealing-wax rubbed in the same way acquires a similar power. We say that the glass and the sealing-wax have become 'electrified'. The kind of electrification is, however, different in the two cases; a piece of electrified glass will repel a similar piece of glass, whilst it will attract an electrified stick of sealing-wax. This has been explained by saying that the glass has taken up a positive charge whilst the sealing-wax is charged negatively; on touching the electrified glass with sealing-wax the charges are neutralized and they both become uncharged. Positive and negative charges are, therefore, to be considered purely as opposites; one is merely the absence of the other, and both together represent an uncharged condition. This type of electricity is called 'static' electricity; it remains stationary, or static, in the body which happens to acquire it. If we

<sup>1</sup> This Chapter may be omitted on the first reading of the book.

## ELECTRICITY AND THE ATOM

make the electric charge move, perhaps by rapidly moving the charged body, then we have dynamic, or flowing, electricity which is able to cause certain definite effects. A current, or flow, of electricity, for example, can produce a magnetic disturbance in its neighbourhood so that a magnetic needle has its equilibrium position altered.

It is possible to produce this flow of electric current by other and simpler means. If a piece of zinc and one of copper, or almost any two dissimilar metals, are placed in dilute sulphuric acid and kept apart in the acid, but are connected by a wire outside, then a magnetic effect is produced in the neighbourhood of this wire. The effect is the same as would be produced if a charge of positive electricity were being moved along the wire from the copper to the zinc plate. This arrangement of zinc and copper dipping in an acid is, therefore, a source of dynamic electricity; it is called a 'voltaic cell' in honour of Alessandro Volta, a Professor of the University of Pavia, who discovered this type of cell at the end of the eighteenth century. The two metal plates dipping into the acid are called poles or electrodes; the one from which the positive

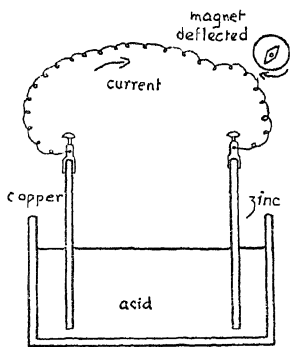


FIG. 2.—A Simple 'Voltaic' Cell

electricity flows *outside* the cell is called the positive and the other the negative pole or electrode. Electricity is a form of energy, and in the voltaic cell it results from a chemical change in which energy is liberated. A cell of this type converts chemical energy into the electrical form. A dynamo can also produce a flow of electric current, and in this case it is a result of the transformation of mechanical energy.

The flow of an electric current through a wire is often compared with the flow of water through a pipe connected with a cistern; the rate at which the water runs out will depend on the head, or pressure of water in the tank and also on the diameter of the outlet pipe. The quantity of electricity which flows through a wire depends in the same way on

the difference of electrical pressure, or electromotive force as it is generally called, between the two electrodes and also on the resistance which the wire sets up to the flow of the current. The electrical resistance depends on the dimensions of the material and also on its nature. A long wire will have a greater resistance than a short one, whilst a thick wire offers less resistance than a thin one. Materials which have a low resistance, metals for example, are said to be good conductors of electricity, whilst non-metals generally have a high resistance and are bad conductors. The amount of current flowing is usually measured in terms of units called 'ampères', the electromotive force (E.M.F. for short) is measured in 'volts' and the resistance in 'ohms'; for a given electrical circuit these quantities are connected by Ohm's Law which says that the current (C) flowing through a circuit is proportional to the E.M.F. (E) applied and inversely proportional to the resistance (R). Expressed in terms of symbols the law tells us that,  $E = CR$ .

Air and other gases are very poor conductors, and in order to make a current pass through them a very high E.M.F. is required, and even then there is usually only a sudden surge of current in the form of a spark. If the air or gas is put into a closed glass vessel connected with a pump, and two metal plates, as electrodes, sealed in at the ends so that they can be attached to a source of current, some interesting phenomena may be studied. It was noticed as far back as the middle of the nineteenth century that as the gas is pumped out, that is the pressure is reduced, a luminous discharge of electricity of quite a new kind can be made to pass through the gas even without using a very high E.M.F. As the pressure inside the tube is reduced still further the character of the discharge changes and a point is reached at which there is only a very faint luminosity within the tube, but the glass walls glow with a greenish phosphorescence. By placing various obstacles within the discharge tube it was found that the glow was produced by a stream of rays sent out in straight lines from the electrode connected with the negative pole of the source of current. This electrode is called the cathode and hence the rays were called 'cathode rays'.

It was shown later that these rays could be diverted from their original tracks by means of a magnetic field and hence particles carrying an electric charge, found to be negative,

must be in the rays. Subsequent investigation showed that the cathode rays were simply a stream of negatively charged particles, called electrons, moving with a very high velocity—from 10,000 to 100,000 miles per second—depending on the E.M.F. applied and the pressure and nature of the gas in the tube. The mass or weight of each electron was found to be only one eighteen-hundredth part of the weight of a hydrogen atom the extreme lightness of which has already been mentioned in the previous chapter. The electrons are so small, too, that one hundred thousand of them would have to be placed side by side in order to stretch right across one single molecule! These electrons, always with the same negative charge and the same mass, can be obtained with any gas in the tube and with any electrode material, and hence in 1897 Professor (later Sir) J. J. Thomson suggested that they are present in all forms of matter; thus the electron came to be regarded as one of the units from which the atom itself was built up.

Now matter is generally electrically neutral and hence when the negatively charged electrons were produced in the discharge tube there had to be corresponding positive particles. Goldstein, a German physicist, had observed that if holes were made in the cathode then rays apparently coming from the other electrode, called the anode, could be observed streaming through the channels formed. These anode rays were found to consist of positively charged particles. Experiments, by J. J. Thomson and by Aston of Cambridge, on the deflection of the positive or anode rays in electrical and magnetic fields have made it possible to determine the weights of these particles. The results of this work show that the positive charge is always attached to the atoms or molecules of gas present in the tube through which the discharge of electricity is passed; the positive particles, unlike the electrons, have never been obtained apart from matter. This suggested, therefore, that matter was made up of a massive positive unit and a number of extremely light negative electrons which balance the electric charge exactly but contribute very little towards the total weight. Further experiments have confirmed this point of view.

In 1895 Röntgen noticed that when the gas in the discharge tube ceases to glow and the walls of the tube are phosphorescing certain new rays were coming from the walls *outside* the tube. These rays were called Röntgen or X-rays; they did not consist of charged particles nor were they material, but



they had a remarkable power of penetrating many substances which were opaque to ordinary light. Further examination showed that the rays were similar in nature to light waves ; that is, they were vibrations in the ether but with very short wave lengths. In general it was found that X-rays could be obtained whenever cathode rays impinged on some solid object and so the general method of producing X-rays is to introduce a special target, or anti-cathode, in the path of the cathode rays. It was observed that the particular character of the X-rays as measured by the wave length, or the frequency, which is inversely proportional to the wave length, of the most prominent rays varied with the nature of the anti-cathode. Moseley, in 1913, whilst studying these characteristic X-rays, as they were called, made a most important discovery ; he found that the frequency of the ray was directly connected

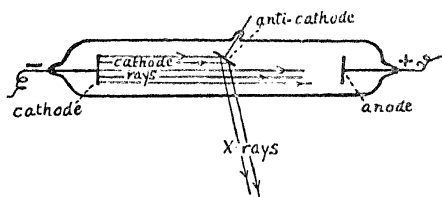


FIG. 3.—Diagram of Discharge Tube for the Production of Cathode rays and X-rays

with the atomic number (p. 17) of the anti-cathode material, and by measuring this frequency it was possible to determine the atomic number of an element quite independently of any knowledge of its atomic weight. Owing to the fact that the number of missing elements was not known at the time the atomic numbers of some elements were uncertain, but the work of Moseley cleared up the difficulty and he showed that uranium, the element with the highest atomic weight, had an atomic number of 92. Hence only 92 elements can exist between and including hydrogen and uranium, and as 90 have apparently been identified there only remain two to be discovered.

Contemporaneously with the work on X-rays some remarkable discoveries were being made in the field of radioactivity. In 1896 Becquerel noticed that uranium salts were able to emit certain rays which can affect a photographic plate even

when wrapped in black paper that was quite opaque to ordinary light. This property proved to belong to the uranium atom and to be present in all uranium compounds. Two years later it was found by M. and Mme. Curie that uranium minerals contained an element which gave off these radiations to a much more considerable extent than uranium itself; this new element was called 'radium' and the property of emitting these rays was called radio-activity. It was found subsequently that a number of other elements, for example thorium which is used in making gas-mantles, also possessed this curious power of producing rays more penetrating than ordinary light.

On examining the radiations coming from the radioactive materials it was found that they could be divided into three groups which have been called alpha ( $\alpha$ ), beta ( $\beta$ ), and gamma ( $\gamma$ ) rays, from the first three letters of the Greek alphabet. The  $\alpha$ -rays were found to carry a positive electric charge and to have a mass four times as great as that of the hydrogen atom; this happens to be the mass of the helium atom, and in fact Professor (now Sir Ernest) Rutherford was able to prove that the  $\alpha$ -rays were made up of positively charged helium atoms moving with a very high velocity. This remarkable result suggested that certain radio-active atoms, at least, if not others, contained helium atoms as units in their structures. The  $\alpha$ -rays could be detected by the scintillations, or small flashes of light, which they were found to produce when they struck a screen coated with zinc sulphide or other chemical substances. The  $\beta$ -rays were shown to be very similar to the cathode rays produced in the discharge tube and to consist of electrons moving with high speeds, whilst the  $\gamma$ -rays were found to be vibrations in the ether similar to X-rays; in fact the  $\gamma$ -rays are always associated with  $\beta$ -rays just as X-rays are connected with cathode rays.

Rutherford and Soddy in 1903 put forward a most revolutionary theory to account for the phenomenon of radio-activity; they suggested that since all the radio-elements have high atomic weights the atoms are becoming complex—top heavy, so to speak—and unstable with the result that they undergo a process of spontaneous disintegration. As a consequence of this disintegration the  $\alpha$ - or  $\beta$ - particles are emitted and an entirely new atom—of a new element with distinct physical and chemical properties—results. This new atom is in its turn unstable and breaks up with the emission of its char-

acteristic type of radiation. This process of disintegration continues through a number of stages until an atom is reached which happens to have a stable structure ; this element is called the end-product of the radio-active series and does not give off any radiations. The loss of an  $\alpha$ -particle, with a mass of four units, will mean that the atomic weight of the new element will be 4.00 less than that of its parent atom, whilst the loss of a  $\beta$ -particle hardly affects the weight appreciably. This remarkable theory of radio-active disintegration is certainly in agreement with the known facts and although at the beginning of the present century an atom was regarded as something immutable and permanent yet we now believe that these radio-elements, although quite definitely elements, are *spontaneously* disintegrating into simpler elements ; this implies, of course, that elements are made up of the same fundamental units which we have reason to believe are simply positively and negatively charged particles. It is interesting to note that the rate at which the radio-active elements break up cannot be influenced at will in any known way ; attempts have been made to affect it by using very high and very low temperatures and high and low pressures, but the radio-atom still disintegrates at its own rate.

The theory of disintegration has been put to a very interesting test. Uranium has an atomic weight of roughly 238 and is the parent of a series of radio-elements ; during the process of disintegration eight  $\alpha$ -particles are lost and so the end product, which an extension of the theory incidentally tells us should be identical with the element lead, should have an atomic weight of  $238 - 8 \times 4.0$ , that is 206. On the other hand the radio-element thorium with an atomic weight of roughly 232 is the parent of another and independent series ; before the end product is reached six  $\alpha$ -particles are lost and again the last member of the series should be identical with lead. The atomic weight of the end product of this series should be  $232 - 6 \times 4.0$ , that is 208. Now it is an interesting fact that lead is found in nature associated both with uranium and with thorium minerals ; this lead was extracted in the form of its salts which were most carefully purified and the atomic weight of the element determined. The results obtained from this work indicated that the atomic weight of the lead associated with, and probably derived from, uranium was very close to 206, whilst that associated with

thorium, although quite pure and chemically identical with the other form of lead, had an atomic weight of nearly 208 ! These remarkable results are in agreement with the disintegration theory and afford for it very strong support. Ordinary lead, not associated with any radioactive material, has an atomic weight of 207.2 and is thus mainly a mixture of the two forms which are found separately in thorium and uranium minerals. These two forms are called 'isotopes' ; they have exactly the same chemical properties and the same atomic number as determined by their characteristic X-rays (p. 30) but they differ in their atomic weights. The work of Aston on positive or anode rays (p. 29) produced when different elements, or their compounds, are present in the discharge tube, indicates that quite a number of the non-radioactive elements are actually mixtures of two or more isotopes with identical chemical properties but with different atomic weights. Chlorine with an atomic weight which is accurately known to be 35.46 has been found to be a mixture of isotopes of atomic weights 35.0 and 37.0 in the proportion of roughly four to one respectively, thus making up an average of about 35.46. In this way it has been shown that many of the elements which apparently have fractional atomic weights actually consist of a number of isotopes each one having an atomic weight which is practically a whole number, provided that the atomic weight of hydrogen be taken as 1.0077. This suggests, to some extent, that the hydrogen atom may possibly be one of the units in atomic architecture.

Although there have been many general indications concerning the connexion between electric charges and the structure of atoms we have not yet given any definite information which suggests how these electric charges in the atom are arranged. Some experiments by Rutherford in 1911 threw very considerable light on this problem ; he allowed a stream of  $\alpha$ -rays to pass through a thin sheet of metal and followed the tracks of the rays by watching the scintillations produced on a zinc sulphide screen. It was observed that by far the largest proportion of the alpha particles apparently travelled in almost straight lines, but a few appeared to be violently deflected from their original track. In order to account for this observation Rutherford suggested the ' nucleus theory ' of the atom which is the one generally accepted at the present day. According to this theory the positive charge on an atom is concentrated on a

very small nucleus upon which resides almost the whole of the weight of the atom, whilst the negative electrons are arranged in some way around the nucleus. The atom has often been compared with the solar system ; the sun corresponds to the positively charged and massive nucleus, whilst the planets, moving in their orbits, correspond to the almost weightless electrons. The space in which the comparatively small number of electrons move is equal to the whole volume of the atom, but as the electrons and the nucleus are only about one hundred-thousandth part of the diameter of the atom itself it is evident that most of the atom, like the solar system, consists of empty space.

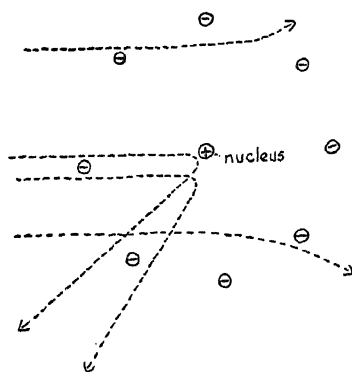


FIG. 4.—The Scattering of  $\alpha$ -rays

The dotted lines indicate the paths of the  $\alpha$ -particles through an atom. (The arrangement of the outer electrons is imaginary)

Now when an  $\alpha$ -particle, which is quite small, is shot through a number of atoms the probability is very much in favour of its passing clean through in a straight line ; if it happens to meet an electron, then owing to the small mass of the latter the comparatively heavy  $\alpha$ -particle will simply push it away without itself, so to speak, 'turning a hair'. But if by any chance the  $\alpha$ -particle should approach the nucleus of the atom its positive charge will be strongly repelled by the

positively charged and comparatively massive nucleus, and so a small proportion of the  $\alpha$ -particles, about 1 in 10,000, will be considerably deflected from the original direction of motion. The nucleus theory is thus in agreement with Rutherford's observations and also with the fact already mentioned that we can never seem to get a positive charge free from matter, or appreciable mass, whilst the electron is apparently purely a negative charge.

The work of Rutherford and others has indicated further that the *net* number of unit positive charges on the nucleus is equal to the atomic number of the element, and since the atom as a whole is electrically neutral there must be an equal number

of negative charges, or electrons, in the surrounding orbits. This means, of course, that the atomic number is a very important property of the atom and this is in agreement with Moseley's observations (p. 30) on the characteristic X-rays. In fact, we now believe that the chemical properties of an element depend entirely on the net number of positive charges on its nucleus and not so much on its atomic weight; the isotopes of a given element all have the same atomic number.

According to the theory outlined the atom of hydrogen, the simplest and lightest of all atoms, consists of a nucleus with a mass 1.0072 and carrying a unit positive charge, whilst a solitary electron, of mass about 0.0005, revolves unceasingly round it in a comparatively vast empty space. If the hydrogen nucleus were magnified so as to be the size of a halfpenny then the electron would appear like another halfpenny moving at a tremendous speed—millions of miles per second—about a mile away! The single positive charge carried by the nucleus of the atom of hydrogen is regarded as the unit of positive electricity and is called the 'proton'; it is always associated with a mass of 1.0072. The next atom, helium, has a nucleus of mass 4.00 with a net positive charge of two, and the same number of nuclear electrons. Judging by the mass, the helium nucleus must contain four protons, since each proton has a mass of roughly 1.00, but as it only has a net positive charge of two, there must also be two negative electrons in the nucleus; these so-called 'cementing' electrons are supposed to hold the nucleus together. It should be noted that theoretically the mass of the helium atom should be four times 1.0072, for the four protons, plus four times 0.0005 for the total of four electrons, that is 4.0308, whilst the actual mass is 4.00. In the formation of an atom of helium, therefore, from four protons an amount of mass 0.0308 units is annihilated! This seems rather remarkable, especially as we have always been led to believe that matter is indestructible; we always imagined that matter could be changed from one form to another but never destroyed!

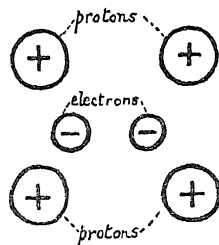


FIG. 5. — Diagrammatic Representation of a Helium Nucleus

The modern view, however, is that matter is purely a manifestation of electric charges and these are merely a form of energy (p. 27) and so when mass is destroyed energy must be liberated in its place. On this basis it has been calculated that in the course of the formation of one ounce of helium from hydrogen there would be enough energy set free to supply 1 million horse-power for seven years ! It is very possible that this change from hydrogen to helium is going on in some of the stars and the tremendous amount of energy liberated would account for their enormously high temperatures. On the earth, however, we cannot see how to make four hydrogen nuclei and two cementing electrons hold together to form a helium nucleus. Although, as Andrade says, 'perhaps we shall one day get, with great difficulty, a few atoms of helium so to form, which will satisfy the man of science ; perhaps we shall get a controlled rate of formation which will satisfy the engineer, perhaps we shall get an uncontrolled and cumulative rate of formation which . . . will destroy the world and satisfy nobody'.

We have already mentioned that nearly all atoms have whole number weights and so in the formation of any of these from protons there must be a vast liberation of energy. In fact if matter, which is merely electricity, could be annihilated in any way energy would be set free ; it is the dream of the scientist to be able to tap this source of power and it is often said that the next age of energy will be that of Atomic Energy. In this connexion Sir William Bragg says : ' I am of opinion that atom energy will supply our future need. A thousand years may pass before we can harness the atom, or to-morrow may see us with the reins in our hands.' Who knows ?

On the basis of the concepts expressed above it is possible to obtain an idea of the construction of any atom ; take, for example, the heaviest of all—uranium—with an atomic weight of 238 and an atomic number of 92. The nucleus must evidently contain 238 protons, to account for the weight, and also 146 electrons, so as to leave a net positive nuclear charge of 92 ; there will also be this number (92) of electrons moving in a series of orbits surrounding the nucleus. It is fairly clear that such a complex nucleus may be unstable and it does, in fact, disintegrate, as we have already seen, and emits an  $\alpha$ -particle consisting of four protons and two electrons, that is a helium nucleus. A new atom with a new atomic number, 90,

and a new atomic weight, 234, results ; this in turn emits an electron ( $\beta$ -particle) from its nucleus yielding still another atom with the same atomic weight but an atomic number of 91, and so on throughout the series. If two atoms have the same *net* nuclear charge but contain a different number of protons and cementing electrons then they are isotopes with the same atomic number but different atomic weights. The two isotopes of lead, for example, contain 208 and 206 protons (each with a unit positive charge and a mass of roughly 1.00) respectively, but the nucleus of the former contains 126 cementing electrons whilst the latter has only 124 ; thus the net nuclear charge, and hence the atomic number, is 82 in each case, although the atomic weights will be 208 and 206.

We have already mentioned that the  $\alpha$ -particle is probably one of the units of atomic structure ; we can put this in other words by saying that the nuclei of the more complicated atoms contain helium nuclei, each consisting of a group of four protons and two electrons and having a mass of 4.00, as structural units. Since atomic weights are not all multiples of 4.00 the nuclei must contain a number of protons, mass 1.007, in addition to make up the necessary amount ; this fact has been verified by Rutherford's recent work. He found when swift  $\alpha$ -particles are passed through certain elements that protons moving with high speed are liberated ; they are probably knocked out of the atomic nucleus by the force of impact of the  $\alpha$ -particle.

Let us consider this matter a stage further ; what is left of the atom when the proton is detached ? Take the case of aluminium, as a random example ; this element has an atomic number, and hence a net nuclear charge, of 13. When it is bombarded by  $\alpha$ -particles a few aluminium atoms each lose a proton and the resulting nucleus now has a net charge of 12 and hence it is that of a new atom with an atomic number of 12. This happens to be magnesium, and so we have deliberately been able to transmute one metal, aluminium, into another, magnesium, although only to such a minute extent that it is impossible to detect the magnesium chemically ; we believe, however, that if our theory is correct it must be formed. So after 2,000 years the dream of the alchemist is being realized, but on a scale so small that it would hardly have satisfied or convinced any of the earnest seekers after gold. It is worth noting that a few years ago German and Japanese scientists



claimed to have converted mercury into gold by subjecting the former to a very intense electrical discharge ; the difference between these two metals is ultimately a matter of one proton and an electron, and a very strong electrical field might conceivably have removed them. Consequently the claims were seriously entertained by scientists for some time, but it has been shown since that the gold detected was probably present all the time in some part of the apparatus. Even though the transmutation may not have been accomplished the possibility was taken seriously ; so we are back in a new age of alchemy, but our main objective now is the search for truth and not for gold.

Before leaving the subject of atomic structure we should just deal briefly with the problem of the arrangement of the orbital electrons—those outside the nucleus—the number of which is equal to the atomic number of the element. The most promising theory in this connexion is that of Bohr, a Dane, who first suggested it in 1913 while he was working with Rutherford at Manchester. According to the theory it is considered that all the electrons rotate round the nucleus but that each electron has a number of possible stable orbits. As long as the electron rotates in one or other of these orbits it neither absorbs nor emits any radiations, but if it passes from one stable orbit to another it will emit rays of a definite wave length which depends on the positions of the two orbits concerned. This definite radiation corresponds to a definite line in the spectrum of the element, which is obtained when the light emitted by the element under suitable conditions is analysed and split up by a spectroscope ; every possible pair of orbits gives a definite line in the spectrum. The single electron of hydrogen has apparently about thirty possible orbits and hence its spectrum should consist of over 400 lines ; some of these will be in the range of visible light, some in the range of short-wave, or ultra-violet light, and others correspond with heat radiations or infra-red rays. Many of the lines have been detected and the wave lengths of the rays producing them are in agreement with the formula deduced by Bohr. In a more complicated atom there are, of course, a large number of possible electron orbits and hence a vast number of spectral lines ; in such cases other factors, which we are unable to discuss here, also enter.

The original theory of Bohr was devised mainly to account

for the spectra of elements and hence it threw no light on the purely chemical properties of the atom. Two American scientists, Lewis in 1916 and Langmuir in 1919, developed what may be called the chemist's arrangement of electrons. According to their theory the electrons tend to arrange themselves in a series of groups, corresponding with the groups or periods, found when the elements are arranged in order of increasing atomic weights (p. 17). The successive and completed stable groups were believed to contain 2, 8, 8, 18, 18, and 32 electrons respectively. On the assumption that all atoms tended to form, as far as possible, a stable and complete group, or sheath, of electrons Langmuir was able to account for many of the chemical properties of the elements, and also for their valency (p. 24) which was regarded as due to the sharing of electrons between the atoms. This theory satisfied the chemist but was of little value to the physicist who was chiefly interested in spectrum lines. In recent years, however, scientists have combined the theory of the moving electron—Bohr's theory—with the idea of arrangement in definite groups, but new concepts concerning the electron which are being developed may necessitate a complete revision of our views.

This brief, and consequently incomplete, account of the modern position with regard to the problem of the structure of the atom will indicate how gleams of information obtained from a large number of different lines of experiment have been brought together to throw some light on what at first appeared to be an insuperable problem.

#### QUESTIONS

1. What is the difference between static and dynamic electricity?
2. How may the flow of an electric current be compared with the flow of water?
3. Describe briefly the phenomena of the 'discharge tube', and compare them with those of radioactivity.
4. Outline the present-day idea of the structure of the atom.

#### SUBJECTS FOR ESSAYS AND DISCUSSION

1. The possible consequences of the discovery of a method of utilizing atomic energy.
2. The relationship between matter and energy.
3. The importance of the atomic number.
4. The existence of lead isotopes as evidence for the disintegration theory of radioactivity.

### FURTHER STUDY

1. The history of the discovery of the voltaic cell.
2. The work of Crookes on the discharge of electricity through a rarefied gas.
3. Radioactivity.
4. The spectra of elements.

### BOOKS TO READ

Stars and Atoms. Eddington. (Oxford Univ. Press.)  
The Interpretation of Radium. Soddy. (Murray.)  
The ABC of Atoms. Russell. (Routledge.)  
The Electron. Millikan. (Univ. of Chicago Press.)  
Atoms and Rays. Lodge. (Benn.)  
Chemistry in the Twentieth Century. Chapter by Andrade. (Benn.)  
Modern Scientific Ideas. Lodge. (Benn.)  
The Atom. Andrade. (Benn.)  
New Worlds for Old. Lunn. (Methuen.)  
Radioactivity. Fajans (translated by Wheeler and King).  
(Methuen.)

### SUGGESTIONS FOR EXPERIMENTS

Observations on static electricity.  
Make a voltaic cell and observe the magnetic effect of the current.  
Electrical discharge through a rarefied gas.  
Use of the spectroscope.  
Visit the Science Museum, South Kensington, when in London.

## CHAPTER IV

### THE AIR AND ITS GASES

**A**LTHOUGH the air is invisible as well as tasteless and odourless, we know from its effects that it must be something material ; the force of the wind is alone sufficient to prove to us the existence of air. Two thousand years ago Hero, of Alexandria, proved that air was material by inverting a vessel with only one opening in water ; the water did not enter the vessel and hence the latter could not have been really empty. When another hole was made in the top of the vessel the water rushed in and the air could be felt streaming out from this new opening. Since air is a form of matter, it has weight ; a vessel full of air weighs more than the same vessel after the air has been removed by a pump. Just as a piece of wood which is lighter than water will rise to the surface and float, so anything lighter than air will rise and float in the air. A balloon or airship filled with helium or hydrogen—the lightest gases known—will, therefore, rise unless deliberately held down. The weight of the air is indicated by the height of the mercury in a barometer ; when we say that the barometer reading is 30 inches, we mean that the total weight of air above a certain area of the earth's surface—say one square inch—is equal to the weight of a column of mercury 30 inches in height with a cross-sectional area of one square inch.

The actual weight of air over every square inch of the surface of the earth is nearly 15 pounds. Water vapour weighs less than the same volume of air and so when the air is damp the height of the barometer decreases ; a falling barometer, therefore, generally indicates that rain is probable. The envelope of air which surrounds the earth completely is called the 'atmosphere' ; it is densest near the surface of the earth and gradually gets more rarefied as we ascend. At a height of  $3\frac{1}{2}$  miles the density of the air is reduced to one-half, at 7 miles

to one-quarter and at 60 miles to about one forty-thousandth of its value at the surface. The upward extent of the atmosphere is, theoretically, unlimited, although at a height of about a hundred miles there is probably less air than in a good vacuum produced by an air pump. The composition of the air also varies with the height ; naturally the lightest constituents will be present in a larger proportion at the higher levels.

It has already been mentioned in the discussion of the supposed elementary nature of air (p. 9) that it is chiefly a mixture of the two gases oxygen and nitrogen ; it will be interesting to describe some of the results which led to this

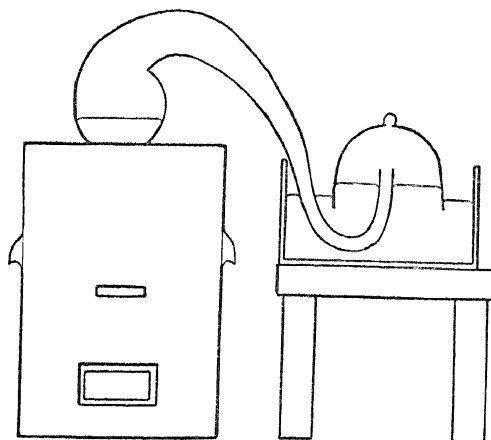


FIG. 6.—Sketch of the Apparatus used by Lavoisier for heating Mercury in an enclosed Volume of Air

conclusion. Probably the most convincing experiments were made by Lavoisier after he had heard of Priestley's discovery of oxygen in 1771. Lavoisier heated some pure mercury (quicksilver) in a closed vessel of air for twelve days ; the original volume of the air was 50 cubic centimetres (c.c.), but at the end of the period of heating the volume had decreased by  $7\frac{1}{2}$  c.c. The residual air was found to be no longer fit for burning or breathing, whilst part of the mercury had been converted into a red powder or calx. On separating the calx and heating it,  $7\frac{1}{2}$  c.c. of gas, which was exactly the volume by which the original air had been diminished, were set free, and

pure mercury was left. From the observations of Priestley, it was known that this gas was much more adapted for burning and respiration than was ordinary air, and hence Lavoisier concluded that it was the active constituent of air. On mixing the  $7\frac{1}{2}$  c.c. of this active gas with the  $42\frac{1}{2}$  c.c. of the inactive gas which remained after heating the mercury, 50 c.c. of ordinary air were reproduced. This proved fairly conclusively that air was a mixture of an active gas which was called oxygen and an inactive constituent, later called nitrogen. The active constituent is apparently used up in burning, breathing, in the rusting of a metal or when it forms a calx as a result of heating in air. By burning phosphorus in air it can be shown that the inactive residue, mainly nitrogen, constitutes roughly 79 per cent. by volume, whilst the remaining 21 per cent. is oxygen.

The question is often asked : Is air a mixture or a compound of oxygen and nitrogen ? Although a number of compounds of oxygen and nitrogen are known, air is *not* one of them ; it is undoubtedly a mixture of the two gases, and some of the reasons for this conclusion can be given. Firstly, we have already seen (p. 16) that chemical compounds always have exactly the same composition, but samples of air obtained from different places often show quite appreciable variations in composition. In the second place when two substances combine together chemically, that is when a chemical change occurs, there is frequently a liberation or absorption of heat (p. 94) ; when oxygen and nitrogen gases are mixed in the proportion of 1 volume to 4 volumes—the ratio in which they are present in air—there is no noticeable heat change. Thirdly, the properties of air are the average of those of its constituents, whereas in a compound we find entirely new properties. For these and other reasons, therefore, we say that air is a mixture.

Although oxygen and nitrogen are the main constituents of the air, it has been found that they are not the only constituents ; as a result of burning of wood, coal, oil, etc., and the respiration of animals and human beings, the oxygen of the air is replaced to some extent by carbon dioxide and water vapour ; these two substances are, therefore, always present in the air. Carbon dioxide also results from fermentation and putrefaction processes which are continually occurring, whilst water vapour will naturally be produced by evaporation from

the areas of water which cover a large part of the earth's surface. It will be explained later (p. 101) how plants play an important part in preventing the unlimited accumulation of carbon dioxide in the air and a balance results ; as a consequence the carbon dioxide content of the air rarely varies from 3 or 4 volumes per 10,000 of air. The quantity of water vapour in the air at any place depends on the nature of the climate and the geographical features of the situation.

In 1784 an English scientist, Henry Cavendish, who was related to the family of the Duke of Devonshire, made a very interesting observation during the course of his experiments on air ; unfortunately he was of a retiring and uncommunicative nature—a scientific recluse, in fact—and probably for this reason his important conclusion attracted no attention for over a hundred years. Cavendish mixed ordinary air with oxygen and passed a series of electric sparks through the mixture ; in this way the oxygen and the nitrogen were made to combine chemically to produce a substance called nitrogen dioxide, and this could be removed by means of a dilute alkali. The experiment was continued until there was no further diminution in volume, that is when presumably all the nitrogen had been removed. 'Liver of sulphur' was then admitted and this absorbed all the remaining oxygen, 'after which', says Cavendish, 'only a small bubble of air remained unabsorbed, which certainly was not more than  $1/120$ th of the bulk of the phlogisticated air (i.e. nitrogen) let up into the tube ; so if there is any part of the phlogisticated air of our atmosphere which differs from the rest . . . we may safely conclude that it is not more than  $1/120$ th part of the whole'.

No attention appears to have been paid to this statement that a small part of the inactive constituent of the air might not be nitrogen, until 1893 when the late Lord Rayleigh, a physicist of considerable eminence, published the results of some very accurate measurements which he had made on the densities of gases. He found that the nitrogen gas obtained from air after the removal of oxygen and other obvious impurities, was about 1 part in 200 heavier than an equal volume of perfectly pure nitrogen which had been obtained from chemical sources. Although this difference was small it was quite definite and far exceeded the possible errors of Lord Rayleigh's accurate experiments, and hence had to

have some definite meaning. In a communication to the scientific weekly journal *Nature*, Lord Rayleigh asked for suggestions as to possible explanations for the difference between chemical and atmospheric nitrogen, but for some time, in spite of Cavendish's observations of the previous century, there was no reply.

Shortly afterwards, Professor (later Sir William) Ramsay, of University College, London, commenced an investigation of the problem. He knew that nitrogen could be made to unite with heated magnesium metal, and in this way it could be removed from a gas mixture and so after removing the oxygen, etc., from the air it was passed to and fro over heated magnesium in order to remove the nitrogen. Although this process was continued for several days, there still remained behind a small volume of gas which was neither oxygen nor nitrogen; after further treatment by the method of Cavendish, the final residue, which was about one-hundredth part of the volume of the original air, was found to consist of an entirely new and hitherto unknown gas. In August, 1894, at the British Association meeting held in Oxford, Rayleigh and Ramsay made a preliminary announcement concerning their important discovery; they had thus verified Cavendish's remarkable observation—remarkable because it was made at a time when accurate measurement in chemistry was a matter of extreme difficulty.

In due course the new gas was examined and found to be more dense than pure nitrogen, and hence a certain proportion of atmospheric nitrogen—actually 0.94 per cent. by volume—was heavier than a similar volume of the pure chemical gas. One of the most striking properties of the new gas was its incapacity to unite chemically with other substances, and owing to its inert nature it was called 'argon' which meant 'idle' or 'lazy'. As a consequence of this property, and also as a result of its comparative heaviness, argon has found a very important industrial application in recent years; it is used for most of the so-called gas-filled 'half-watt' lamps which have to a considerable extent replaced the less economical vacuum lamps. The argon plays an important part in these lamps because it prevents the tungsten filaments from evaporating and allows the use of a much higher temperature and consequently a greater illuminating efficiency results. The 'tungar' thermionic valve, made in this



country by the B.T.H. Co., contains a tungsten filament in a bulb filled with argon—hence the name; it is in considerable use for the conversion of alternating into direct current for accumulator charging. For these purposes argon is obtained from liquid air; when the latter is allowed to evaporate slowly, the gases which come off first contain a large proportion of argon together with some oxygen. Further purification is generally carried out chemically to remove all of the oxygen as this gas is harmful to the electric lamp filament.

In the course of further experiments during the years 1894 to 1898 on the argon obtained by the complete removal of oxygen and nitrogen from the air, Sir William Ramsay and his co-workers found that there were four other gases which were present to a small extent in the original air. These gases were called helium, neon, krypton and xenon, and together with argon they make up a group of elements known to the chemist as the 'inert gases of the atmosphere'; they are all, like argon, very inactive chemically. The four new gases mentioned are only present to a total extent of about 2 parts in 100,000 parts of air, and hence in spite of the fact that they are present wherever there is air, they must be regarded as comparatively rare. Neon is the most common of the four, and although its only source is the air, of which it constitutes 1 part in 80,000, yet it is a gas of industrial importance. Electrical discharges can pass through neon with great ease, and the gas emits a reddish-orange glow; this fact is made use of in the sparking-plug testers for motor-cars. If the plug is functioning satisfactorily then it can cause an electric discharge to pass through the neon and a reddish flash is seen every time a spark passes. Glowing electric advertisement signs, consisting of thin glass tubes bent into the shapes of letters, also contain neon and make use of the same principle. An electric discharge lamp containing neon has a very penetrating light which may be visible within a range of 30 miles, and hence such lamps are used for beacon lights. Neon is always made from liquid air, but the purification is a matter of some difficulty.

The gases krypton and xenon are only present to the extent of 1 part in 20 million, and of 1 part in 170 million parts of air respectively, and hence are only available in extremely minute amounts. So far these gases have found no industrial

applications. The remaining gas of the series, helium, is a very interesting constituent of the air ; its story forms one of the most remarkable romances of modern chemistry. During the eclipse of the sun which occurred in the year 1868, the spectrum of the sun's chromosphere was examined ; that is the light coming from this portion of the sun was split up into its constituent rays by means of a spectroscope (p. 38). In this spectrum there was observed a yellow line which did not correspond in position with any of the lines produced by the elements known at the time and hence Lockyer and Frankland attributed this new line to an element which was unknown on the earth but was actually present in the sun. For the sake of convenience, this unknown and unattainable element, the existence of which could only be inferred, was called 'helium', from the Greek word meaning 'sun'. Some twenty-seven years later, in 1895, Ramsay, whilst looking for new sources of argon, examined the gas which was given off when the rare mineral 'cleveite' was heated with acid ; he found that it contained some argon as well as nitrogen and hydrogen, but it also showed a brilliant yellow line, not produced by either of these three gases, when examined in the spectroscope. Further comparison showed that this line was identical with the one detected in the sun's chromosphere, and hence the gas obtained by Ramsay from cleveite contained a proportion of the element helium.

The gas helium was also found to be liberated when certain other minerals, for example monazite, which is found in America and is used as a source of thorium for gas mantles, were heated. Shortly afterwards, Kayser detected the presence of helium in the atmosphere and it is now known to be present to the extent of about 1 part in 200,000 volumes of air. Helium we know is one of the products of the disintegration of radioactive elements (p. 31), and this is the source of the gas both in the air and also in the minerals from which Ramsay obtained it. Certain mineral waters which have come into contact with radioactive substances in the earth are charged with helium gas ; the Bath waters are an example of this type, and it has been calculated that the King's Well, in that city, alone evolves 1,000 litres of helium annually. On examining helium gas it was found to be inactive, non-inflammable and second in lightness only to hydrogen, which is the lightest gas known. An interesting consequence of this

lightness is that the gas must be present to a greater extent in the upper reaches of the atmosphere and it has been calculated that at a height of 50 miles the air would probably contain about 4 per cent. of the gas, that is about 10,000 times as much, in proportion, as at the earth's surface.

Until recently the only gas used for filling balloons and airships was hydrogen because this is the lightest of all gases, and it can be made comparatively easily and cheaply. It has the great disadvantage, however, of being inflammable, whilst a mixture of this gas with air, in certain proportions, is liable to explode ; consequently great precautions have to be taken in connexion with flames and engines. Helium, on the other hand, although it has only 92 per cent. of the lifting power of hydrogen, is absolutely non-inflammable and non-explosive. By using this gas for filling airships, the engines could be placed in the gas envelopes and certain advantages of structure obtained ; further, the loss of gas by diffusion through the material of the gas-bag should be decreased by at least one-third. Unfortunately the rarity of helium made it appear to be a chemical curiosity and not a gas which could ever be turned to practical use on a large scale.

During the war airships and balloons filled with hydrogen were particularly dangerous as they were exposed to gun and rifle fire often with incendiary bullets, and so various scientists thought of the possibility of making use of helium in place of hydrogen. In 1916, however, only about 30 cubic feet of fairly pure helium were available in the whole world, and the cost, if it had been purchasable, would have been about £400 per cubic foot. The smallest useful balloon has a gas-bag holding about 17,000 cubic feet, and so the cost of filling even this would have been over £6,000,000, while the cost of filling airships containing over 1 million cubic feet of gas, even if the gas had been available, would have been impossibly great. It was known, however, that certain natural gases which came up from the earth in Canada and in the U.S.A. contained frequently 0.5 to 1 per cent. of helium, and hence towards the end of 1915, Sir Richard Threlfall persuaded the Board of Invention and Research of the British Admiralty to investigate the possibility of extracting fairly pure helium from this gas ; soon afterwards scientists in the United States also began to work on the same problem.

After much experimental work from 1915 to 1918, a satisfactory method of extraction was invented which depended on the fact that helium is the most difficult of all gases to liquefy; by the use of low temperatures and high pressures it was possible to liquefy all the other constituents of the natural gas except the helium, and after passing through various stages it was obtained in an almost pure condition. By the time the armistice was signed in November, 1918, about a quarter of a million cubic feet of purified helium had been obtained at an average cost of about £100 per 1,000 cubic feet; fortunately the war ceased and the gas was not required for military purposes.

Since 1918 the process of extracting helium from natural gas has been greatly improved, so that at the present time it can be obtained at a cost of about £7 per 1,000 cubic feet. It is extremely probable that the development of aerial navigation will mean an increased demand for helium owing to the absolute safety from fire and explosion which its use gives; unfortunately the initial cost of gas is much greater than in the case of hydrogen, although it is possible that there may not be such an appreciable difference in the ultimate cost. The hydrogen of an airship or balloon has to be entirely renewed eight or ten times a year when in regular use because some of the gas becomes replaced by air and a dangerous explosive mixture is formed in the gas-bag; helium, on the other hand, does not form such an explosive mixture and in any case the purification of the gas from the admixed air, which is very dangerous in the case of hydrogen, can be carried out quite readily with helium. A possible economy may also be effected by mixing the helium with one-fifth of hydrogen; the resulting gas is still non-explosive, but is much cheaper than pure helium and has a slightly greater lifting power. Two obvious disadvantages of helium must be pointed out; in the first case the gas-bag must be about one-tenth larger than when hydrogen is used, and secondly, arrangements must be made to compress the gas into cylinders when it is desired to reduce the lifting power, whereas hydrogen, being much cheaper, is allowed to escape. As a result of a test flight made in the U.S.A. towards the end of 1921 in a helium-filled airship, it was reported that a greater speed was attained and the ship manœuvred better than when filled with hydrogen. On the other hand it has been reported

recently from Germany that airships using hydrogen gas can be navigated more easily than those using helium; it is possible, however, that this opinion may be connected with the fact that the chief sources of helium to-day are in the U.S.A. and in Canada.

Helium has one or two other interesting applications. Tungsten filament lamps used for signalling work contain helium because the light dims rapidly and so it allows quick signals to be sent. It has also been found that the presence of helium in the oxygen breathed by men working under high pressures, as in diving bells and caissons, prevents them from being overcome by 'caisson sickness' which is due to the fact that at high pressures carbon dioxide, the waste product of breathing, cannot be easily eliminated from the blood. Before leaving the subject of the rare gases of the atmosphere it would be well to point out that the story of the three gases—helium, neon and argon—shows in a very striking manner how a purely scientific investigation started by Rayleigh and Ramsay has had important and unexpected practical consequences.

The main constituents of the air—oxygen and nitrogen—are both important technical substances. Oxygen for commercial purposes is produced mainly from liquid air; ordinary air is cooled to a low temperature by special methods and at the same time it is subjected to pressures of about 3,000 pounds to the square inch. Under these conditions it turns to a mixture consisting mainly of liquid oxygen and liquid nitrogen. Of these two liquids, nitrogen has the lower boiling-point and so evaporates off more readily, thus leaving behind a liquid consisting mainly of oxygen. By using this principle it is possible to separate air into oxygen and nitrogen gases pure enough to be used industrially. A certain amount of oxygen is also obtained as a by-product in the manufacture of pure hydrogen from water by an electrical method which will be referred to later (p. 58); this process, however, only supplies less than one-fifth of the world's annual output of over 5,000 million cubic feet of oxygen gas.

All substances which burn in air burn even more vigorously in oxygen and it is upon this fact that the commercial uses of the gas depend. Hydrogen gas and coal gas burn in oxygen more intensely than in air, and by the use of special burners it is possible to burn a mixture of coal gas or hydrogen and

oxygen and so produce a very hot flame. If the flame is allowed to impinge on a piece of lime a brilliant white light is produced commonly known as the 'limelight'; this was used to a considerable extent at one time—before electric lighting became as common as it is to-day—for theatrical illumination and for magic lanterns. If acetylene is mixed with oxygen and burnt in the so-called oxy-acetylene blowpipe

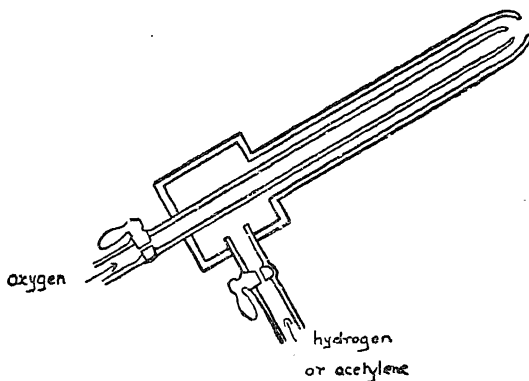


FIG. 7.—Section through a Blow-pipe

the temperature of the resulting flame can reach  $3,000^{\circ}\text{C}$ . or  $5,400^{\circ}\text{F}$ ., and by means of it sheets of steel can be cut through with almost the same ease as cheese is cut with a knife. Nearly 80 per cent. of the oxygen used in industry is actually used for metal welding and steel-cutting by means of the oxy-acetylene flame.

Since oxygen is the gas which is concerned in the process of breathing, it is natural to assume that in pure oxygen life would be more active than it is in air; it is probable, however, that we should have worn out our present systems completely before the age of 20 years was reached. In cases of illness, for example in pneumonia and other lung troubles, in which breathing is difficult and requires stimulation, oxygen is administered and found to be very beneficial. In submarines, where the supply of air is limited, or at great heights—in flying or climbing—where the air is rarefied, oxygen is frequently used as an aid to normal breathing. Divers and mine rescue workers are also often supplied with cylinders

of compressed oxygen to enable them to breathe. These uses, however, account for only a small proportion of the oxygen manufactured every year. A small amount of liquid oxygen is also used in the preparation of some of the 'safety' explosives for mining purposes.

Whilst on the subject of oxygen, it would be appropriate to say a few words about the curious gas ozone to which the health-giving properties of seaside air are so often erroneously attributed. Seaside air probably does not contain more than 1 part in several millions of ozone ; in fact 1 part in 20,000 of air is said to be irritant and poisonous ! A smaller concentration than the latter, however, has the power of purifying air and ozone is actually used for this purpose in crowded meeting halls and in the London Underground Railway. Ozone has the power of killing many bacteria and hence it is used for the purification of the water supplied to some large towns ; this is the chief commercial application of ozone at the present time, but it is also used in small amounts in many chemical processes. Ozone is merely another form of oxygen ; in fact, it may be regarded as oxygen in a concentrated condition. In the ordinary oxygen gas the molecules each contain two atoms and may be written thus :



In ozone, however, we know as a result of chemical and physical experiments that each molecule contains three atoms of oxygen, and so it may be pictured as :



This new molecule has different properties from those of ordinary oxygen ; it tends to give up its third oxygen atom easily and so it has strong 'oxidizing' properties. The chief chemical applications of ozone are connected with this particular property. Ozone is almost invariably produced when an electric discharge of some kind passes through air or oxygen ; in fact, the curious smell of ozone, noted as long ago as 1785, and always to be detected in the vicinity of an electrical machine when in operation, was at one time considered to be the 'smell of electricity' ! In the manufacture of ozone a special kind of electric discharge known as the 'silent, or brush discharge' is used ; if air is passed through the discharge

apparatus then ozonised air results, and this is the form in which ozone is generally used.

Nitrogen is the main inactive constituent of the air, but it is by no means as inactive as the other inert gases of the atmosphere; although it is of no use in burning and in breathing, yet it enters into a number of chemical reactions which yield important products. When we discuss the requirements of the soil for agricultural purposes, we shall see that nearly all plants must be supplied with nitrogen in a combined form; ordinary nitrogen gas, as present in the air, is generally of no direct value in this connexion. The actual methods for making the nitrogen combine with other elements to form products which the plant can use will be discussed later (p. 168), and so at this point we shall only deal with the extraction of the nitrogen from the air. The most common method is to obtain it from liquid air as has already been explained when describing the manufacture of oxygen. Another method which is being developed to a considerable extent is to pass a mixture of air and steam over coke under suitable conditions; air consists of oxygen and nitrogen, steam is a compound of oxygen and hydrogen, and coke consists mainly of carbon and the products resulting in the process are chiefly the gases nitrogen, hydrogen and carbon dioxide. The latter can be removed readily by washing out with water in which it dissolves, whilst the mixture of nitrogen and hydrogen remaining, is used directly in the manufacture of ammonia (p. 169).

Before concluding this chapter on the gases of the atmosphere, it should be stated for purposes of completeness that the gas hydrogen, which will be discussed in greater detail in the next chapter, is present to the extent of 1 part in 10,000 volumes of air near the earth's surface. At higher levels, the air contains a much larger proportion of hydrogen owing to the extreme lightness of this gas; in fact, it has been calculated that at a height of 50 miles above the surface of the earth, more than half of the atmosphere, which is of course extremely attenuated, consists of hydrogen gas.

#### QUESTIONS

1. What are the two chief constituents of the air and in what proportions are they present?
2. Give a short account of the discovery of the inert gases of the atmosphere.



3. Why is air considered to be a mixture and not a compound?
4. What are the chief uses of oxygen and nitrogen?

#### SUBJECTS FOR ESSAYS AND DISCUSSION

1. The study of the rare gases of the atmosphere as an illustration of the unexpected practical consequences of a purely scientific investigation.
2. Lavoisier's work on the composition of the air.
3. The importance of helium and its limitations, with special reference to progress in aerial transport.
4. Imagine the possible consequences of an atmosphere consisting entirely of oxygen.

#### FURTHER STUDY

1. Liquid Air : its preparation, properties and uses.
2. The discovery, isolation and uses of the rare gases.
3. The manufacture, composition and uses of ozone.
4. The variation in the composition of the air in various parts of the world.

#### BOOKS TO READ

The Discovery of the Nature of Air. Taylor. (Bell.)  
The Gases of the Atmosphere. Ramsay. (Macmillan.)  
Chemistry in Industry. Vol. II. (Chemical Foundation, New York.)  
Triumphs and Wonders of Modern Chemistry. Martin. (Sampson Low.)  
Chemistry of To-day. Bull. (Seeley, Service.)  
Books recommended for Chapter I.

#### SUGGESTIONS FOR EXPERIMENTS

The density of air.  
The barometer.  
Preparation and properties of oxygen and nitrogen.  
The composition of the air.  
Examine a blow-pipe.

## CHAPTER V

### WATER AND HYDROGEN

**W**ATER is not only very useful but it is also widely distributed; in the form of seas, rivers and lakes it covers three-quarters of the surface of the globe, and it constitutes on the average about 70 per cent. of all living things. The human body consists of about two-thirds water, and many fruits and vegetables of even more. It may not be surprising to learn that nine-tenths of a luscious strawberry is merely water, but it is often difficult to realize that water constitutes about three-quarters of a fresh potato. Some primitive forms of life, such as jellyfish, may contain as much as 96 per cent. of water, and in this connexion the German scientist Wolfgang Ostwald says: 'These organisms . . . move, swim, eat and make love—and all this with 96 per cent. of water in their affection.'

Water plays an important part in all animal and vegetable life. It is well known that plants cannot live in a dry soil—that is why the Sahara is a barren desert—and that a dry season, from the point of view of the agriculturist, is often more disastrous than a wet one. The dependence of vegetable life on water is due to the fact that plants get an essential proportion of their food from the soil, and this is available to them only in the form of a liquid solution. The various mineral salts present in the earth, such as nitrates, phosphates and potassium salts, dissolve in water, and the soil solution formed in this way is sucked up by the roots and passed into the various parts of the plant where the dissolved matter is utilized in building up the plant structure. Clearly, without water this process could not occur. After the digestion of food, the resulting material cannot pass from the alimentary canal into the blood stream for utilization in different parts of the animal body unless it is in the form of a solution (p. 130); water provides the liquid medium for producing this solution.

The human body, therefore, needs a plentiful supply of water, and this is obtained both in the form of beverages and also as part of apparently solid food such as fruit, vegetables, meat and fish, all of which contain a considerable proportion of water.

The important part played by water in life processes, and the large proportion of this liquid present in all living matter, have suggested the possibility that life originated in the sea, which once covered the whole of the globe. It is at least probable that the reason why water enters so largely into the constitution of living organisms is because it is so extremely common. Some writers suggest that it may be purely a matter of chance that the liquid of our seas happens to be water, and Martin, in his *Triumphs and Wonders of Modern Chemistry*, says: 'If the early seas had consisted of petroleum or alcohol, no doubt forms of life would have come into existence which contained as much of these liquids as they now contain water.' It must be realized, however, that such forms of life would have been very greatly different from life as we know it now.

When we realize the wide distribution of water we can begin to understand why the Greeks regarded it as one of the fundamental constituents of matter; in fact water was considered to be an element almost until the end of the eighteenth century. In 1781 Joseph Priestley made what he called 'a mere random experiment to entertain a few philosophical friends'; he mixed ordinary air with what was called inflammable air, and is now called hydrogen, and passed an electric spark through the mixture. An explosion occurred, and Priestley recorded that he observed the inside of the vessel to become coated with dew. Priestley thought that this dew came from the air, and so he paid no further attention to it. Henry Cavendish, however, thought that the matter was worth investigating; he repeated Priestley's experiment on a larger scale and was able to prove that the dew observed was actually water, and that it had not come merely from the air. Cavendish was able to show that water, and nothing else, was produced when hydrogen and oxygen gases, in the proportion of 2 volumes to 1 respectively, were exploded by an electric spark. Doubt was thus thrown on the idea of the elementary nature of water, and the results of his experiments, published by Cavendish in 1784, suggested that it was a chemical compound of hydrogen and oxygen.

At about the same time Lavoisier, in France, arrived at this conclusion as a result of a series of independent observations ; he found that when steam is passed over red-hot iron the oxygen of the water is removed to form oxide of iron, whilst hydrogen gas is set free. Further confirmation was obtained shortly afterwards by two English scientists, Nicholson and Carlisle ; they noticed that if an electric current from a voltaic battery is passed through water, the latter is split up into its constituent gases. The oxygen gas appears at the positive pole or point at which the current enters the water, whilst the hydrogen is set free at the negative pole at which the current leaves ; the volume of hydrogen liberated is found to be twice that of the oxygen. Thus the composite nature of water was definitely established and we now write the formula of a molecule of water as  $H_2O$ , because we know it to consist of two atoms of hydrogen united chemically with one atom of oxygen. Water, unlike air, is a definite compound ; the union of hydrogen and oxygen to form water is a chemical change in which an entirely new substance — a liquid with distinct properties — is formed and heat is liberated. This liberation of heat may be readily observed ; when hydrogen gas burns in air or oxygen a hot flame is obtained and water is formed. The production of water from its constituent elements provides, therefore, an excellent example of a chemical change.

Both the gaseous constituents of water are of industrial importance ; we have already discussed oxygen and we will now deal with hydrogen. When steam is passed over heated coke (carbon) a mixture of carbon monoxide gas and hydrogen gas results ; the chemist describes the reaction in the form of the simple equation :

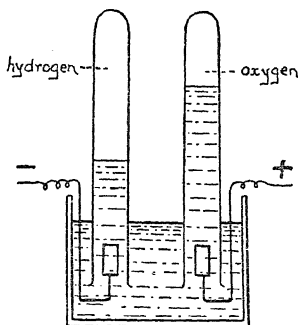
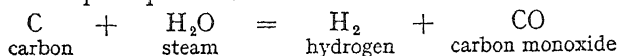
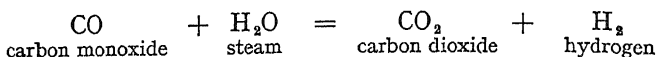


FIG. 8.—The Decomposition of Water into Hydrogen and Oxygen by means of an Electric Current

This mixture is known as water-gas. If excess of steam is used then under certain conditions the carbon monoxide can be made to take the oxygen away from water to produce carbon dioxide and leave hydrogen, thus :



The carbon dioxide is removed by dissolving it in water under pressure, whilst the hydrogen is almost insoluble and so remains behind. This is one important technical process for making hydrogen. Another method is based on Lavoisier's experiment described above (p. 57); steam is passed over red-hot iron and hydrogen results. The oxide of iron formed at the same time is regenerated by passing water-gas over it. For certain industries very pure hydrogen is required, and this is best obtained by passing an electric current through water to which a little alkali has been added; the discovery of Nicholson and Carlisle has thus an important practical application. In the technical process the apparatus is so designed that the hydrogen and oxygen are collected quite separately in an almost pure condition; this not only avoids any difficulty of separating the gases, but also eliminates any danger of the hydrogen-oxygen mixture exploding. Pure oxygen is thus an important by-product of this process for manufacturing hydrogen. In the laboratory, for experimental work, hydrogen is generally prepared by the action of certain metals such as zinc, iron and tin on fairly strong acids like sulphuric or hydrochloric acid. All acids, as a matter of fact, contain hydrogen in a combined form, but it is not always a simple matter to release the gas.

Hydrogen is a colourless gas which burns readily in air with an almost colourless but hot flame; it forms almost half of ordinary coal-gas. With air or oxygen it yields a highly explosive mixture. It is the lightest gas known, and since 1783 it has been used for filling balloons, and more recently for airships. Owing to the risk of fire and explosion involved in the use of hydrogen it is being replaced, in some instances, by the slightly heavier, more expensive, but absolutely inert gas helium (p. 48). Hydrogen gas has many industrial applications. It is used to convert liquid fats such as whale oil, cotton-seed oil and other vegetable oils into solid fats which are required for soap and candle making, and for the

manufacture of artificial lard and margarine (p. 161). These latter substances do not appear to be greatly used in this country, but are commercial products in the U.S.A. Hydrogen is also used to a great extent in the manufacture of ammonia from atmospheric nitrogen (p. 169).

Hydrogen plays an important part in the production of tungsten filaments for use in electric lamps and in wireless valves; in the first place the metallic tungsten is produced from the oxide by the action of hydrogen, and the gas is also used in the complicated process of producing a thin tungsten wire which will not fall to pieces at the high temperature it has to withstand in the lamp or valve. A number of new processes are being developed for the production of a petrol substitute for the internal combustion engine which is so widely used at the present day; nearly all of these involve the use either of hydrogen alone or else mixed with carbon monoxide as water-gas (Chap. XVI). An important chemical objective of to-day is to discover a cheap method for manufacturing hydrogen for use in the preparation of synthetic liquid fuels for motor-car engines.

Water in nature is continually in a state of circulation. Evaporation from seas and lakes and from trees causes an accumulation of water vapour in the upper atmosphere which eventually condenses to form clouds consisting of very small drops of water; when these drops reach a certain size they fall as rain. Much rain falls directly into the seas and oceans, but a great deal also falls on to land areas and either drains straight into a stream or else it soaks into the earth. The underground waters accumulate and soon break their way through as a spring and form a stream; this eventually joins a river on its way to the sea. In the course of this circulation, water helps in the disintegration of rocks, the formation of soil and to a great extent in the making of scenery. The action of water is both mechanical and chemical. The fall of rain helps in the loosening of softer rocks, and as the water flows over the surface of the earth it carries away with it particles of soil and stones. Frost is a very powerful agent for the disintegration of rocks; water gets into rock crevices and in cold weather it freezes. In freezing water expands thus causing the rock to crack, and when the ice melts the pieces of stone fall away. This breaking-up process incidentally lays bare fresh portions of rock so that any soluble

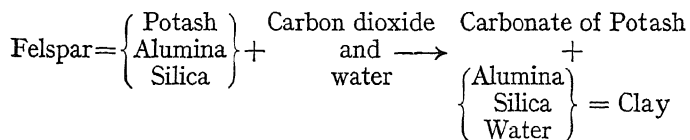
material which it contains may be dissolved out by rain water.

Rivers and glaciers have a definite eroding action on the soil, and in the course of many thousands of years they produce valleys and ravines. Rivers carry a great deal of sediment down with them to the sea ; thus it has been calculated that the Thames carries between 1 and 2 million tons of solid matter, mainly torn off from rocks, to the sea every year, whilst all the rivers of the world carry nearly 6,000 million tons of solid suspended matter. This naturally involves a great deal of wearing down and disintegration. In addition, river water contains considerable quantities of salts which are dissolved out by the continual action of rain and spring water ; it is estimated that the total weight of dissolved matter carried to the sea every year by all the world's rivers, amounts to about 2,500 million tons.

The dissolved material has been accumulating for hundreds of millions of years. Although the sea was at one time almost pure water, it now contains, however, on the average about 3·5 per cent. of dissolved solids, of which roughly three-quarters is ordinary common salt, or sodium chloride ; this accounts for the salt taste of sea-water. Since the dissolved salts cannot get away from the sea, and more is continually being brought down by rivers, it is clear that the sea is getting saltier as time goes on ; owing to the vast volume of water present this increase is not generally noticeable, but it is undoubtedly occurring. We have evidence of it in such inland seas as the Dead Sea ; here the volume of water is limited, and as dissolved matter was being brought down by rivers continuously, a time was reached when the water could not hold all the salts in solution, and so solid deposits began to separate out. The nature of the dissolved salts and the deposit which separates out depends on the kind of soil through which the rivers and streams which feed the inland sea have flowed ; some of these salts, e.g., borax, soda and potash salts, are being developed for industrial purposes in various parts of the world.

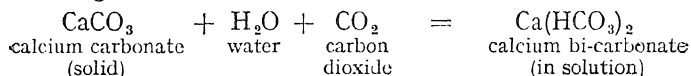
An essential factor concerned in the action of water in nature is the gas carbon dioxide which is always present in air (p. 43). Rain water at first consists of almost pure water, but during its fall to earth it dissolves some of the carbon dioxide gas from the air and more from decaying vegetable

matter in the soil. Although carbon dioxide when dissolved in water forms a solution which is an extremely weak acid, yet the continual action of this solution can, and does, in the course of many years, wear away rocks. Granite, for example, is a mixture or conglomerate of three different substances, quartz, mica and felspar. As a result of the process of 'weathering', chiefly due to the action of water and frost, the granite is broken up into small pieces of its separate constituents. The quartz is disintegrated into small particles and forms sand; quartz and sand are exactly the same chemically, and they are generally known under the heading of 'silica' (p. 12). Felspar is a chemical compound of silica, potash, or oxide of potassium, and alumina, or oxide of aluminium and the chemical action of carbon dioxide and water on felspar may be written thus:



The carbonate of potash is soluble in water and is carried away by it in solution, whilst the compound of silica, alumina and water, which is china clay, remains behind or is washed away from its position of origin and deposited nearby. This explains why clay is always found in the vicinity of granite deposits; for example, china clay is found near the granite of Devon and Cornwall. Water containing carbon dioxide acts in a similar chemical way on other rocks, and this together with the purely mechanical action already described, results in the formation of soil; the nature of the soil will clearly depend on the rock from which it has been formed.

In limestone districts carbon dioxide laden water plays a very important rôle in the formation of scenery as well as in other respects. Pure water is unable to dissolve chalk or limestone—they are both forms of what the chemist calls calcium carbonate (p. 15)—but water containing carbon dioxide has the power of dissolving these substances and the resulting solution contains calcium *bi*-carbonate. Thus:



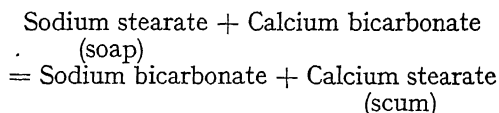


The caves and gorges found in limestone districts, as for example in Somerset and in Derbyshire, have been formed by the dissolving action of water containing carbon dioxide, and although the amount dissolved is very small, yet the continued action during thousands of years has caused very considerable erosion. In these caves there are generally to be seen stalactites growing downwards from the roof, and stalagmites, after many centuries, working their way up from the floor; sometimes the two projections meet and a natural pillar results. These growths owe their formation to the same dissolving power of carbon dioxide laden water. Water containing calcium bicarbonate in solution percolates slowly through the roof of the cave and as each drop hangs before it is large enough to fall, some of the water evaporates and the carbon dioxide gas escapes with it; the calcium carbonate, or limestone, which was dissolved by this water and carbon dioxide can now no longer be held in solution, and hence it is deposited on the roof of the cave. Although each drop only deposits an extremely minute amount of limestone, yet in the course of ages the accumulation is sufficient to give a stalactite of considerable length. Stalagmites are formed in a similar way when the drop of water has fallen from the roof to the floor; evaporation of water and carbon dioxide occurs here too, and so the limestone is deposited and gradually grows upwards. In the famous Cheddar Caves, in Somerset, it is possible actually to see the stalactites and stalagmites in the slow process of formation.

In limestone districts it is natural to expect that spring water, and hence river water, will contain a considerable amount of dissolved calcium bicarbonate. Dolomite limestone contains a certain amount of magnesium carbonate which can be dissolved, like calcium carbonate, by water bearing carbon dioxide and so the resulting solution contains magnesium bicarbonate, as well as the calcium compound. Spring water as a result of its passage through the earth frequently contains also sulphates and chlorides of calcium and magnesium in solution. Water containing considerable amounts of these dissolved salts is harsh to the skin when used for washing, and does not form a lather at all readily with soap; such water is called 'hard' water. Rain water contains no dissolved salts and hence it is called 'soft' water by contrast; it lathers easily with soap, feels pleasant and

is said to be beneficial to the skin. Since the water in limestone districts is invariably very hard the inhabitants find it economical to collect rain water for toilet and laundry purposes. In granite or slate districts or where there is hard sandstone or other such material which is almost insoluble in water even when it carries carbon dioxide, the water will contain very little dissolved mineral or saline matter, and so it is generally quite soft. Domestic water supplies are usually obtained directly from rivers or from lakes, and these collect the spring water from the areas which they drain; the hardness of the house supply will thus depend on the nature of the soil through which the water has passed before entering the reservoir.

In addition to the possible harmful effect of hard water on the skin, it also has a number of economic disadvantages. Let us consider in the first place the wastage of soap which occurs during the formation of a lather. Soap consists chiefly of sodium salts of certain acids, e.g. stearic acid derived from fats (p. 85), and we may take sodium stearate as a typical example of a soap. The calcium and magnesium present in hard water change places with the sodium of the soap and form calcium and magnesium stearates which, being insoluble, are thrown out in the form of a scum which rises to the surface; for example:



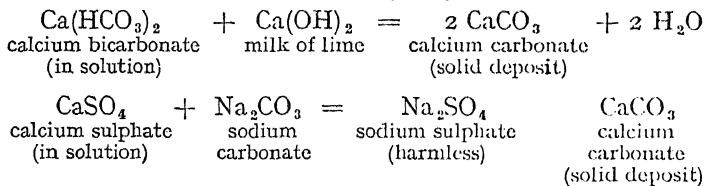
The soap is thus not available for the formation of a lather until a sufficient amount has been added to use up all the calcium and magnesium salts present in the water. This is clearly an extremely wasteful process; in fact, the use of hard water can result in the wastage of about half the amount of soap required for washing purposes.

There is also another kind of wastage which results from the use of hard water. It has already been mentioned when explaining the formation of stalactites, that if carbon dioxide is removed from water the calcium and magnesium carbonates which it allows to be held in solution are thrown out as solid deposits. This process occurs when water is boiled—in a kettle, for example; the carbon dioxide gas is driven out

## IN DAILY LIFE

by the heat and the carbonates are deposited as 'fur'. Hard water is, therefore, the cause of the 'furring' of kettles. The addition of a little acid such as strong vinegar (acetic acid), or spirit of salt (hydrochloric acid), to the 'fur' of a kettle will cause exactly the same effervescence and production of carbon dioxide gas as would be obtained from limestone; this is, of course, due to the fact that 'fur' and limestone are both one and the same chemical substance. If hard water is used in boilers for industrial purposes or for central heating, a thick scale may be formed inside the boiler which will prevent the heat from reaching the water; it has been found that a quarter of an inch thickness of scale requires a 50 per cent. increase in the amount of fuel required for the boiler. Even in the home it is quite noticeable that the water in a furred kettle takes much longer to boil than when the kettle was new. If a boiler becomes 'scaled', then the outside plates have to be raised to a much higher temperature than when free from scale, and so the danger of an accidental burst is considerably increased.

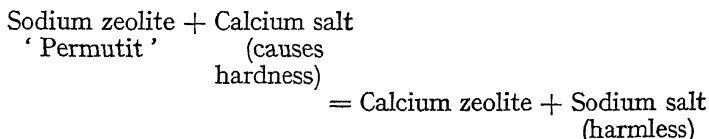
For industrial purposes water is almost invariably softened before it is supplied to boilers; one method of softening is to add a mixture of milk of lime (calcium hydroxide) and soda (sodium carbonate) to the water. These have the effect of removing the carbon dioxide from bicarbonates, and of throwing down all the dissolved calcium and magnesium salts in the form of insoluble carbonates which are allowed to settle before the water passes on to the boiler; in this way scale formation is to a great extent prevented. The chemical reactions which occur in softening may be written thus:



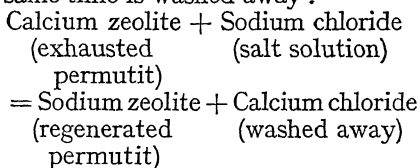
A very ingenious method for the softening of water has been devised in recent years; it is generally known under the name of the 'Permutit' process. This process involves the use of a substance belonging to a group of minerals known as 'zeolites'; a typical zeolite is 'natrolite', a compound of silica, alumina, water and oxide of sodium. The sodium can

## WATER AND HYDROGEN

replace the harmful calcium and magnesium present in hard water, and after such water has passed through a bed of natrolite or sodium zeolite, it contains only sodium salts in solution which do not cause the deposition of scale in a boiler, nor do they prevent the lathering of soap to any appreciable extent. The chemical reaction may be written :



After some time the sodium in the zeolite, or 'permutit' as it is generally called, is all used up, but it can be readily replaced by allowing a strong solution of common salt—that is sodium chloride—to flow through it. The sodium of the salt enters the permutit and regenerates the sodium zeolite once again ; the calcium chloride which results at the same time is washed away :



Such a regenerative process is very cheap and is carried out quite simply ; one supply of 'permutit' can thus last for many years if properly treated. The 'permutit' method of water softening can be applied either on a very large scale for industrial purposes or on a small scale for domestic water supply. It is so simple to operate that during the last few years a number of installations have been erected in large private houses, hotels and in institutions ; where the water is very hard and a

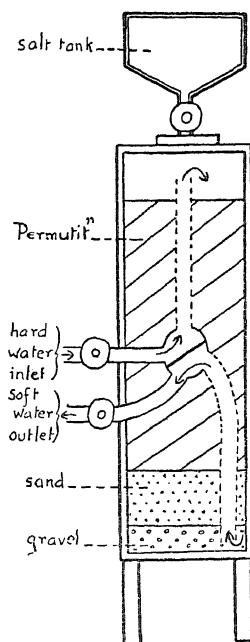


FIG. 9.—Sectional Diagram of a 'Permutit' Water softening Apparatus

great deal is used for cooking and toilet purposes, there is no doubt that considerable economies can be effected by this simple and efficient water-softening process. It has been stated that hard water containing calcium salts—or lime salts as they are commonly called—is harmful for people with rheumatic tendencies and some medical men recommend small 'permutit' installations in the homes of such persons. The increased demand for zeolites as a result of the increasing popularity of the 'permutit' process, has resulted in the development of methods for the preparation of artificial zeolites; these are just as efficient as the natural substance for the softening of water.

It should be mentioned that soft water is required in industry for purposes other than use in boilers; for dyeing, tanning, paper making and in the scouring of textiles, soft water is essential, and both of the processes already described are used for these purposes. It is sometimes asked if it would not be possible to soften water on a large scale at the reservoir, as this would probably be much more economical than a large number of smaller installations. There is one very serious objection to this: water is usually supplied to houses through lead pipes, and these are attacked by soft water. The water would thus contain a very small quantity of lead, not enough to act as a poison outright, but in a sufficient amount to accumulate and produce lead poisoning after a time. Hard water does not dissolve lead to any appreciable extent owing to the formation of a protective coating in the pipes, and, therefore, in districts where the water is naturally very soft it is often deliberately hardened, or else if possible mixed with hard water, in order to reduce the action on the lead pipes.

In the home, for toilet and laundry purposes, water is softened on the small scale by boiling and by adding washing soda or borax. By boiling, the hardness due to bicarbonate—called the temporary hardness—may be removed since the resulting carbonates are thrown out of solution as 'fur'. The so-called permanent hardness, however, due to sulphates and chlorides of calcium and magnesium, can be removed most conveniently and cheaply by means of washing soda (sodium carbonate), although borax is sometimes used. Washing powders and bath salts generally consist mainly of sodium carbonate, in some form or another, sometimes coloured

and scented ; these substances act merely by softening the water.

The supply of pure water free from disease germs to large towns is a matter of prime importance in connexion with the preservation of the health of the people. As a general rule water from a number of rivers and streams is collected in an artificial reservoir, or else in a lake like Thirlmere, for example, which is the water reservoir for Manchester, and then purified. Even if precautions are taken to avoid the entry of sewage or farm refuse into the water supply, there is always bound to be a certain amount of decaying vegetable or organic matter present washed down by the rivers on their way to the reservoir. The organic matter provides food for various kinds of micro-organisms, some of which may definitely be harmful to human life, and consequently special steps have to be taken to remove bacteria, etc., from the water before it is supplied for domestic use. In the first place the water is allowed to stand or else to flow through a tank in such a way that there is the least possible movement ; this allows a great deal of the suspended matter to settle down to the bottom of the tank. The process is sometimes aided by adding to the water alum or the closely related aluminium sulphate ; either of these substances will interact with the salts generally present in water to form a gelatinous precipitate of aluminium hydroxide. This has the power of dragging down with it a considerable proportion of the very finely divided suspended matter which would otherwise take a very long time to settle.

The next stage in the purification is the filtration of the water through sand and gravel ; the filters are made up of several layers consisting of fine sand, coarse sand, fine gravel, small gravel and finally at the bottom broken stone, or gravel, and porous tiles. In passing through these layers all the remaining suspended matter is left behind and also a large proportion of the bacteria and other micro-organisms originally present. After a time the top of the filter bed becomes covered with a coating of slime in which bacteria can breed ; the top layer is then removed and the sand well washed before being replaced. If the original water had been contaminated with sewage—a distinct probability when the water supply is drawn from a fairly large river—the filtered water may still contain some harmful bacteria, and so a final purification is carried out by means of chemical sterilizers or

disinfectants. The substances generally used are either chlorine gas, bleaching powder—which readily liberates chlorine—or ozone; after this treatment the water is as free from bacteria as is reasonably possible, and is fit for domestic use. In small towns and villages where the purification of water may not be carried out efficiently, it is advisable to boil the water before use in order to kill all micro-organisms. The only safe test for good water is, of course, the bacteriological one for the number of microbes present, but a fairly good idea may be obtained by means of chemical tests; if water is found to contain either ammonia or nitrates, then we can be sure that it has been in contact with decaying organic

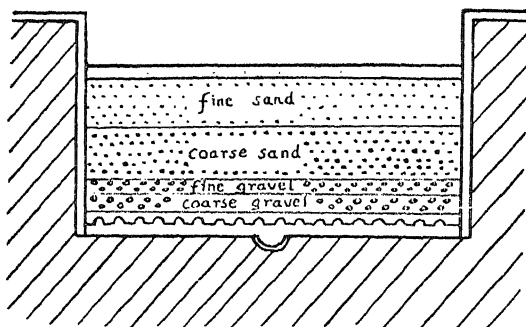


FIG. 10.—Filter-bed for the Purification of Drinking Water

matter, and hence may be dangerous unless special precautions are taken.

For some purposes particularly pure water, free from all dissolved salts, is desirable; this is specially the case in the making up of medicines and for diluting accumulator acid. Such pure water may be made by boiling ordinary water and condensing the steam by passing it through a tube surrounded by a jacket of cold water; the liquid which condenses is known as *distilled* water, and is perfectly pure. Rain is, of course, an example of natural distilled water; the vapour coming from the seas, lakes, trees, etc., is condensed into liquid in the colder regions of the atmosphere. Distilled water, like water which has been boiled, has a 'flat' taste; this is because all the gases have been boiled out. By pouring distilled water, or boiled water, from one vessel to another several times,

it can dissolve a certain amount of air, and the normal taste is restored. Spring water and certain mineral waters, such as Seltzer and Appolinaris, consist of water which is supercharged with dissolved gas, generally carbon dioxide, under pressure, and so they have a sparkling taste. Artificial sparkling water of this kind—known as 'soda-water'—is made by dissolving carbon dioxide gas in water under a pressure of four atmospheres, that is about 60 pounds per square inch; on releasing the pressure, when the bottle of soda-water or syphon is opened, the excess of gas bursts out and produces effervescence or 'fizzing'.

It may be mentioned in conclusion that other natural waters exist in addition to these waters charged with carbon dioxide; their particular properties are connected with the nature of the soil through which the water passes. At Harrogate we have the so-called sulphur waters which contain small quantities of the evil-smelling gas known as sulphuretted hydrogen; these waters are said to have medicinal properties. Chalybeate waters, such as occur at Tonbridge, contain an iron salt—iron carbonate—in solution and are said to be useful for anæmia. Bath waters, recommended as part of the treatment for rheumatism, contain amongst other substances, radioactive materials; whilst Vichy water is an alkaline water which is said to help to reduce the acidity of the blood.

#### QUESTIONS

1. Why is water important in life processes?
2. Account for the origin of hard water. Why is natural water not always hard?
3. How may hard water be softened?
4. How was the composition of water determined?

#### SUBJECTS FOR ESSAYS AND DISCUSSION

1. Water as a solvent in the home and in nature.
2. The economic aspects of the softening of water in the home and in industry.
3. The influence of water on the formation of soil and scenery.
4. The technical applications and manufacture of hydrogen.

#### FURTHER STUDY

1. The distribution of water in Nature.
2. The solvent action of water and the age of the earth.
3. The treatment of water for drinking purposes in your town.
4. The origin and uses of mineral waters and salt lakes.



## BOOKS TO READ

- The Composition of Water. Partington. (Bell.)  
Everyman's Chemistry. Hendrick. (Univ. of London Press.)  
Triumphs and Wonders of Modern Chemistry. Martin. (Sampson  
Low.)  
Chemistry in Industry. Vol. II. (Chemical Foundation, New  
York.)  
Romance of Chemistry. Foster. (Allen and Unwin.)  
Chemistry in the Home and Community. Beery. (Lippincott.)  
Outlines of Industrial Chemistry. Thorp and Lewis. (Macmillan.)  
The Age of the Earth. Holmes. (Benn.)

## SUGGESTIONS FOR EXPERIMENTS

- The electrolysis of water.  
The preparation and properties of hydrogen.  
The solvent action of carbon dioxide in water.  
The softening of water.  
Experiments with soap solutions.  
Preparation of distilled water.  
A visit to the waterworks.

## CHAPTER VI

### CARBON: THE ELEMENT AND ITS OXIDES

**I**N addition to the elements oxygen, nitrogen and hydrogen, already discussed in connexion with the subjects of air and water, there is another substance which is of great importance in our daily lives: this is the element carbon. This element occurs in all living organisms and is contained in almost all products of human, animal or vegetable life; it is also the main constituent of our chief fuels, coal and oil. Carbon enters into so many different combinations with other elements, that more than 200,000 different carbon compounds are known, and these are studied as a special branch of chemical science called 'organic chemistry'. Although the name suggests that the so-called 'organic' compounds are obtained from living organisms, this is not actually the case; the majority of these substances are prepared artificially in the laboratory and many of them do not exist at all, as far as we are aware, in Nature.

The element carbon occurs naturally in the free and uncombined state in two distinct forms: these are diamond and graphite or black lead. It seems very remarkable that the diamond, which is probably the hardest substance known, and graphite, which is a soft flaky material used for the best lead pencils and even as a lubricating agent, should consist of one and the same element, but there is no doubt about this fact. Each consists of the same carbon atoms, and nothing else, but the atoms are built up differently in each case so as to produce substances differing in appearance and in physical properties. These two different forms of the same element are known as 'allotropic' modifications; oxygen and ozone are also allotropic modifications of the one element. Phosphorus, too, exists in distinct allotropic forms; one of these is yellow, catches fire very easily and is poisonous, whilst the other is red, inflames with difficulty and is non-poisonous. Carbon

exists in another form in addition to diamond and graphite ; charcoal, made by burning wood or sugar, is an almost pure form of carbon which differs considerably in appearance from the other modifications of the element. At one time this was regarded as a third allotropic form, but it appears very probable that charcoal really has the same ultimate internal structure of carbon atoms as graphite although the external appearance may be different. The identity of the three forms of carbon may be shown in a number of ways ; a definite weight of diamond, graphite or pure charcoal can be burnt in a good supply of oxygen and in each case there will be obtained the same weight of carbon-dioxide and nothing else.

Towards the end of the last century Moissan, a French chemist, made a mixture of sugar, charcoal and iron and heated it up to  $3,000^{\circ}\text{C}$ . in an electric furnace ; the molten mass was then cooled by plunging it into liquid lead at a temperature over  $2,500^{\circ}$  lower. After a time when the whole mass had solidified the iron was dissolved away, and there remained behind some graphite and a few tiny crystals. The latter were thought to be diamonds, but recent work has shown this not to be the case. If a diamond is heated for some time in the absence of air it may be converted into a coke-like substance, whilst anthracite coal or coke, which consist mainly of carbon, may be heated in an electric furnace to  $3,500^{\circ}\text{C}$ . to produce graphite. This is, in fact, the commercial method for manufacturing graphite ; a certain amount of oxide of iron or silica is added to aid the process of conversion.

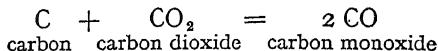
Graphite is used for making 'lead' pencils, metal polish, heat-resisting crucibles and also as a lubricant for low temperature work. Diamond is used chiefly as a gem and to some extent as a cutting material. Black or dark grey diamonds are useless as jewels, but owing to their extreme hardness they are mounted in the faces of rock-drills and are used when boring for oil or water ; the powdered material is also used for grinding and polishing glass, metals and other diamonds. Various other forms of carbon are of commercial importance ; charcoal, probably on account of its great porosity, has the power of absorbing various gases and fumes. This fact is made use of frequently for removing unpleasant odours and noxious gases ; the most efficient respirators used during the Great War contained charcoal, made by burning coco-nut shells, which absorbed the poisonous gases. Certain forms of

charcoal are used to absorb and save some of the gasoline from the so-called ' casing-head ' gas which collects at the head of an oil-well. Bone-black, or animal charcoal, made by distilling bones in closed retorts, is very useful as a decolorizing agent, and it has been in use for many years for the purpose of clarifying sugar syrups. Lamp-black, or a modified form known as carbon black, is a form of soot which is obtained from a smoky flame ; it is frequently observed in the chimney of a paraffin lamp, and hence its name. It is prepared commercially by burning turpentine or tar or natural gas in a limited supply of air, and is used, amongst other purposes, as a pigment in printer's ink, stove polish, carbon paper, type-writer ribbons, gramophone records and as a filler for rubber used in making tyres.

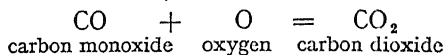
Coke and gas carbon are both fairly pure forms of carbon which are obtained from coal. When coal is heated, or carbonized, in retorts vapours are given off from which coal gas is obtained whilst a residue known as coke is left behind (p. 190). Some of this coke is obtained as a by-product in the manufacture of gas and is sold as a fuel for coke-stoves, whilst a kind of hard coke is specially made for use in metallurgical processes, such as the extraction of iron from its ores. In Great Britain about 20 million tons of coal are carbonized each year for the production of metallurgical coke, whilst another 17 million tons are used in gasworks, thus producing a total of about 25 million tons of coke ; in the U.S.A. about double this amount is made annually. After a retort has been in use some time for the carbonization of coal a hard greyish-black deposit forms round the walls ; this is removed by chipping and is an almost pure and hard form of carbon known as gas-carbon. It is a good conductor of electricity and is used for making the carbon rods for electric arc lamps and for Leclanché and dry electric batteries.

It has been already mentioned that if any form of carbon is heated in a good supply of oxygen, or air, it produces carbon dioxide gas ; each molecule of this gas contains 2 atoms of oxygen to 1 atom of carbon, and so it is given the formula  $\text{CO}_2$ . If, for some reason, there is an insufficient supply of oxygen available some or all of the carbon atoms may only get one atom of oxygen, and so the compound  $\text{CO}$ , or carbon monoxide gas, results. This substance is also obtained when carbon dioxide is passed over heated carbon ; the oxygen of the carbon

dioxide then becomes shared between two atoms of carbon thus :



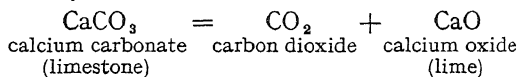
The blue flame which is frequently observed at the top of a coke fire, and sometimes with a coal fire, is due to the burning of carbon monoxide which is produced in this way. Carbon dioxide is formed at the bottom of the grate where the air enters, and on passing through the upper layer of hot coke (carbon) it is converted into the monoxide. When this gas reaches the air at the top of the fire it burns with a blue flame to form carbon dioxide, thus :



If the chimney draught happens to be poor, or the ventilation bad, then some of the carbon monoxide may escape unburnt into the room, and since it is colourless and odourless, but very poisonous, its presence may not be detected until a fatality has occurred. In fact, there have been many deaths due to carbon monoxide produced by charcoal fires burning in badly ventilated rooms ; at one time carbon monoxide poisoning was a fashionable way of committing suicide ! The poisonous action of the gas is due to the fact that it unites chemically with the hæmoglobin—or red colouring matter of the blood corpuscles—and so prevents the body from obtaining the oxygen which is so essential to life and which is usually carried by the hæmoglobin (p. 100). Although carbon monoxide is a gas which can be made fairly cheaply and which gives out a good deal of heat when burning, yet owing to its poisonous nature, and the difficulty of detecting its presence, it is not used to any appreciable extent for domestic heating and lighting. Ordinary coal gas generally contains 10 to 15 per cent. of carbon monoxide, but the characteristic smell of the coal gas is so definite that an escape can usually be detected long before the proportion of monoxide in the air has reached dangerous limits. Carbon monoxide is formed to some extent in the petrol motor, or internal combustion engine, and passes out through the exhaust ; this is particularly the case if the ' air strangler ', which cuts down the air supply, happens to be in use. It is therefore dangerous to stay in a closed garage whilst a motor-car engine is working ; in fact, a neglect of the precaution to ventilate garages has resulted in a number of deaths.

Although carbon monoxide is not used to any appreciable extent in domestic heating, it is used considerably as a fuel gas in industry. If a limited supply of air is passed through a thick layer of hot coke, a mixture of nitrogen and carbon monoxide results; this is known as 'producer' gas, and is used for heating the retorts for making coal gas. Producer gas is readily and cheaply made and it forms a convenient method of heating, since the burning of gas is easier to control than the burning of solid fuel; in order to get the best efficiency it is essential, however, that the producer gas should be burnt very close to the 'producer' in which it is made, in order to avoid any loss of heat. If steam is blown through incandescent coke, water gas, a mixture of carbon monoxide and hydrogen, results (p. 57); both these gases can burn in air with the evolution of heat and so the mixture is a cheap and useful fuel gas. A certain amount of water gas is almost invariably mixed with coal-gas, but the poisonous nature of the carbon monoxide sets a limit to this. Sometimes air and steam are blown through hot coke at the same time, and the resulting gas, which is a combination of producer gas and water gas, known as semi-water gas, is also used as an industrial fuel.

If carbon, carbon monoxide, or any carbon compound is burnt completely in air or oxygen then carbon dioxide results; the gas is one of the products of respiration and decay of animal and vegetable matter. It was discovered in 1616 by van Helmont, who showed that it could be obtained when wood charcoal was burnt in air; hence he called it 'gas silvestre' (i.e., wood gas) because he thought it was present in the wood. The same gas was also obtained when grape-juice fermented and when acetic acid was allowed to act on calcium carbonate. Chalk, limestone, marble and sea-shells are all forms of calcium carbonate, and any one of these when acted upon by acid causes effervescence and produces carbon dioxide gas. It can also be made by heating limestone to a high temperature; this is the method which is frequently used industrially. In this reaction the calcium carbonate splits up into carbon dioxide and calcium oxide, or lime, thus:



The carbon dioxide liberated during the fermentation of 'wort' is collected in the breweries, compressed so that it liquefies,

stored in strong steel cylinders and sold ; this gas is generally used for making the so-called ' aerated ' or artificial ' mineral ' waters (p. 69). Carbon dioxide plays an important part in the baking of bread and cakes. If yeast is used, then the carbon dioxide gas resulting from fermentation produces a large number of gas bubbles in the dough and so causes the porosity aimed at in baking (p. 104). With baking powders the carbon dioxide is generally produced from a mixture of bicarbonate of soda and an acid substance like tartaric acid, cream of tartar,

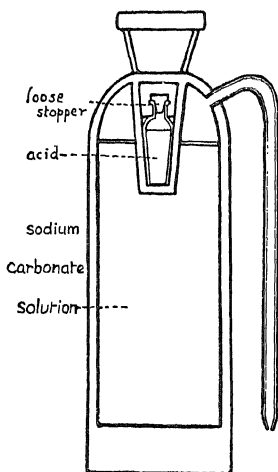


FIG. 11.—A Carbon-dioxide Fire Extinguisher

alum, or calcium biphosphate ; these do not react in the dry state but liberate gas when moistened by the water in the dough. Bicarbonate of soda and sour milk, containing lactic acid, are sometimes used together for baking purposes, because the mixture readily evolves carbon dioxide gas. So-called effervescent ' health salts ' and Seidlitz powders also consist of a dry mixture of bicarbonate and an acid substance, which produces an effervescence of carbon dioxide gas when added to water. Another use for carbon dioxide which may develop in importance is as a refrigerating agent ; the gas can be readily liquefied and then frozen into a snow-like solid, sometimes called carbon dioxide ' snow '. This solid produces a much lower temperature than does ice and it has the additional advantage that when it warms up it simply produces a gas which can be readily dissipated, whilst ice on melting produces water which may soak and spoil the material being cooled. Solid carbon dioxide for this reason is called ' dry-ice ' and its use as a refrigerant is increasing, especially in the United States.

Carbon dioxide is a heavy gas and does not support combustion or burning, and hence it is used for extinguishing fires ; the apparatus generally consists of a metal vessel containing a

alum, or calcium biphosphate ; these do not react in the dry state but liberate gas when moistened by the water in the dough. Bicarbonate of soda and sour milk, containing lactic acid, are sometimes used together for baking purposes, because the mixture readily evolves carbon dioxide gas. So-called effervescent ' health salts ' and Seidlitz powders also consist of a dry mixture of bicarbonate and an acid substance, which produces an effervescence of carbon dioxide gas when added to water. Another use for carbon dioxide which may develop in importance is as a refrigerating agent ; the gas can be readily liquefied and then frozen into a snow-

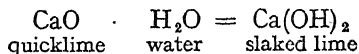
solution of sodium carbonate with a glass tube of sulphuric acid suspended inside. When required for action the tube containing the acid may be broken by means of a plunger, or else the apparatus is inverted ; the mixing of the acid and the sodium carbonate produces a stream of carbon dioxide gas which issues, together with some liquid, from the nozzle and extinguishes the flame.

We shall see later that burning and breathing are very similar processes, and hence the presence of more than a certain proportion of carbon dioxide in the air not only will put out a fire, but it can produce suffocation because oxygen is kept away. After an explosion in a coal mine the air contains a dangerous proportion of carbon dioxide gas and probably carbon monoxide, too ; this is known to miners as 'choke damp', and it has often been responsible for taking the lives of those who have survived the explosion, as well as of numbers of the rescue party. Sewers often contain carbon dioxide, which accumulates from the decomposing matter, and tests have to be made by means of a candle, from time to time ; if a candle will burn, then the air is safe to breathe. Carbon dioxide is one of the products of breathing, and hence in a crowded room it may accumulate to a dangerous extent ; satisfactory ventilation, however, easily avoids the possibility of this occurrence.

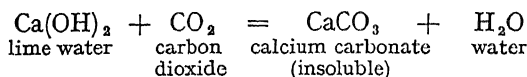
Carbon dioxide gas can dissolve in water to an appreciable extent and the resulting solution has feebly acid properties ; it is said to contain carbonic acid. This acid gives rise to a series of salts (p. 14) known as the 'carbonates' ; of these the calcium salt, calcium carbonate, is probably the best known. It is found in Nature as chalk, limestone and marble ; it is also the material of which pearls, coral, egg-shells and sea-shells are made. Chalk and limestone have been formed as a result of the deposition at the bottom of the sea of myriads of tiny shells ; as a consequence of earth movements these layers were probably compressed together, and then raised above the level of the sea and so chalk hills and limestone deposits were formed. The chief uses of calcium carbonate, in one form or another, are for the production of cement, for the extraction of iron from its ores in the blast furnace (p. 203), and for making lime which is used in the preparation of whitewash, distemper paints and mortar. Crushed limestone or lime are often used for neutralizing the acidity of a sour soil and supplying calcium



for plant growth (Chap. XIV). It has already been stated that by heating limestone or chalk very strongly lime is produced ; this process is carried out in lime-kilns of various types. The product obtained is known as 'burnt lime' or 'quick lime'. If water is added to quick lime it swells up, liberates a large amount of heat and produces 'slaked lime' ; the chemical action which occurs may be written thus :



If slaked lime is made into a thin paste with water we have 'milk of lime', whilst the clear liquid which results when a little slaked lime is added to much water is called 'lime water' ; this solution has alkaline properties and has the power of neutralizing acids. One of the most interesting examples of this neutralization occurs when the acid is carbonic acid ; if carbon dioxide is passed into lime water then the latter is neutralized and the salt calcium carbonate results according to the equation :



We know that calcium carbonate is insoluble in water, and hence it is thrown down as a white precipitate when lime water is exposed to carbon dioxide. This fact is made use of to test for the presence of carbon dioxide gas ; if it is passed into lime water, the latter turns milky owing to the production of the white insoluble calcium carbonate. In this way we can show that carbon dioxide results from breathing—by exhaling into lime water—and in burning—by shaking up lime water in a closed vessel in which a candle has been burning.

Another very important salt of carbonic acid is sodium carbonate, generally known as 'washing soda' or just 'soda' ; this substance is not only used as the basis of washing powders and bath salts, but it is required in many industries, amongst which may be mentioned particularly the manufacture of glass. Soda is found in Nature as a deposit from certain lakes ; the most important of these is Lake Magadi in Kenya Colony, where the soda deposits are now being worked up commercially. It is probable that the salt lakes of Egypt formed the first sources of soda, but another source was later discovered in the substance known as '*barilla*', made from the ash of certain

plants growing on the sea-shore. This ash was used chiefly for the manufacture of soap and glass, but the amount available was very limited. The supply was eked out, to some extent, by means of the salt potassium carbonate, closely allied to soda ; it is generally known as 'potash', since it was originally obtained from the ash of wood which had been used for heating pots. Unfortunately potash, although it was originally used in soap making, does not give such a firm soap as does soda, hence the latter was preferred for the manufacture of this cleansing material.

Towards the end of the eighteenth century the shortage of soda became rather serious, and so in 1775 the Academy of Paris offered a prize to the inventor of a process for making soda (sodium carbonate) from common salt (sodium chloride). In 1791 the French chemist Leblanc proposed a solution to the problem, and in 1793 he started a factory for the manufacture of soda ; unfortunately France was passing through troubled times and a few years later Leblanc's factory was confiscated and the inventor, of what was later found to be a most useful process, died by his own hand, a disappointed man. A short time after, the manufacture of soda by the Leblanc method was commenced in England and proved to be so successful that it held its ground for over a century ; only in the last year or two has it been almost completely, if not entirely, superseded. The Leblanc process consisted firstly in heating common salt (sodium chloride) with sulphuric acid, when sodium sulphate, or salt cake, was produced, whilst a considerable amount of hydrochloric acid gas was allowed to pass into the atmosphere. The salt cake was then mixed with limestone and coal, and on heating a mixture of sodium carbonate and calcium sulphide resulted. The former was extracted by dissolving it in water in which it is readily soluble, and on evaporating the solution soda crystals were obtained. The residue of calcium sulphide was known as 'alkali waste' and for many years was thrown away, only to accumulate and form an evil-smelling dump ; this was one of the nuisances associated with the manufacture of soda. The problem of the disposal of the waste was eventually overcome, to the profit of the industry, when a process was invented for extracting sulphur from it.

The hydrochloric acid gas evolved in the first stage of Leblanc's method for making soda, which later saved the

process from extinction, very nearly ruined it at the commencement. When discharged into the air its poisonous and corrosive nature caused the destruction of all vegetable matter within a considerable radius of the works, and also the gradual eating away of ironwork in the vicinity. There was a great popular outcry against this nuisance and soda manufacturers were forced to absorb the gas in water and so they produced hydrochloric acid solution, generally known as 'spirit of salt'. A hundred years ago, however, there was practically no use for this commodity, and so the manufacturers, naturally having no desire to accumulate the acid, discharged it into rivers with disastrous effects on fish life. The position was becoming extremely unpleasant when the repeal of the paper duty in 1861 completely altered the situation: the increased demand for paper meant that more bleaching agents were required to whiten the raw material used in the manufacture. One of the best bleachers, generally called 'bleaching powder', could be made from the hydrochloric acid by-product of the soda factory, and so a market was found for this troublesome substance.

The creation of a definite demand for the acid gave an additional stimulus to the Leblanc process, and when the modern 'ammonia-soda' or Solvay method was started about fifty years ago it was only the great value of the by-products which saved the older process from complete eclipse. In recent years the new method has been improved to such an extent that it has gradually replaced the Leblanc process, and the latter is only used for the definite purpose of making the small amount of hydrochloric acid required for various chemical manufactures. Even for this purpose the old process is not likely to last much longer, as new methods are being developed for making the acid. Bleaching agents are now made by other methods not involving hydrochloric acid, and so there is little demand for the latter.

Soda is almost exclusively made at the present time by the so-called Solvay process; although the method was devised by two English chemists in 1838 and a factory was started in Whitechapel, London, it was some time before the technical difficulties were completely overcome; even to-day, after many years of practical experiments, improvements are still being made. In brief this method for making soda consists in passing carbon dioxide gas, made from limestone, into a strong

solution of common salt which is saturated with ammonia gas ; after a short time bicarbonate of soda is deposited from the solution. The solid bicarbonate is removed, dried and sold as such, or else it is heated very strongly when it yields a concentrated form of soda known as 'soda ash' ; this is dissolved in hot water and on standing and cooling the resulting liquid deposits soda crystals, or washing soda.

## QUESTIONS

1. What is meant by the term 'allotropic modification' ?
2. For what purposes are the various forms of carbon used ?
3. How may it be proved that diamond, graphite and charcoal are all forms of the same element ?
4. How would you test for the presence of carbon dioxide gas ?

## SUBJECTS FOR ESSAYS AND DISCUSSION

1. The manufacture and uses of water gas and producer gas.
2. The applications of carbon dioxide in daily life.
3. The manufacture of soda.
4. The causes and prevention of carbon monoxide poisoning.

## FURTHER STUDY

1. The preparation of artificial diamonds.
2. The construction of fire extinguishers.
3. The use of carbon in gas masks.
4. The leavening of dough.

## BOOKS TO READ

Concerning the Nature of Things. Bragg. (Bell.)  
Chemistry in Modern Life. Arrhenius. (Chapman and Hall.)  
The Romance of Chemistry. Foster. (Allen and Unwin.)  
Romance of Modern Chemistry. Philip. (Seeley, Service.)  
Triumphs and Wonders of Modern Chemistry. Martin. (Sampson, Low.)  
The Alkali Industry. Partington. (Baillière, Tindall, Cox.)

## SUGGESTIONS FOR EXPERIMENTS

Examination of forms of carbon.  
Preparation of charcoal, animal charcoal, lamp black and coke.  
Burning of carbon.  
Identity of various forms of calcium carbonate.  
Preparation, properties and test for carbon dioxide.  
Observation of a coke fire.

## CHAPTER VII

### CARBON : GLASS, SOAP AND HYDROCARBONS

**A**N important use of soda is in the manufacture of glass, and although glass does not actually contain any carbon it will be convenient to consider it at this point. The story which is usually told concerning the discovery of glass is one due to Pliny; he relates that some Phœnician sailors whilst cooking their food on a sandy shore rested their pots on lumps of 'nitrum', which was probably an impure natural form of soda. The heat of the fire is supposed to have caused the 'nitrum' and the sand to unite chemically and form a glass. This story is probably the result of imagination, as it is very unlikely that the heat of the fire would have been sufficient to have brought about the necessary chemical action between sand and soda. It is certain, however, that glass has been known for at least 5,000 years. Egyptian tombs, dating back as far as 3000, or more, B.C., contain representations of glass blowers at work, whilst glass vessels have actually been found during excavations. In later times, in the days of the Cæsars, the manufacture of glass-ware was taken up on a large scale by the Romans, and these people were probably the first to use glass for windows. In England it appears that glass was not made to any appreciable extent until the thirteenth century, but at that time the demand for stained glass for church windows may have stimulated its production in this country.

Considered chemically glass is a mixture of a number of different silicates; these are salts derived from silica (p. 12). Pure silicates, as a rule, are of no use as commercial glasses; for example, if sand is heated strongly with sodium carbonate there results sodium silicate, which is generally known as 'water glass'. As its name implies it is soluble in water, and hence it is of no value as a glass, but it is used, amongst other purposes, for preserving eggs, for finishing off concrete

## GLASS, SOAP AND HYDROCARBONS

work, for adhesives, and in certain soaps and washing powders. A mixture of sodium silicate and calcium silicate, however, can yield a cheap glass known as 'soda-lime glass', which is used for windows and bottles. This glass is made by heating together a mixture of soda, limestone and sand in suitable proportions, to a temperature of about  $1400-1500^{\circ}\text{C}.$ ; after some time a clear molten mass is obtained which on cooling sets to a colourless glass, provided the raw materials were fairly pure. The carbon present in the soda is evolved as carbon dioxide gas. If any appreciable amount of iron is present then the glass has a greenish tinge which may be neutralized to some extent by adding oxide of manganese to the molten mixture. Green bottle glass is generally made from impure raw material and may contain six or more per cent. of iron oxide which is responsible for the colour.

If the calcium oxide, or lime, in soda-lime glass is replaced by lead oxide, then we get the so-called 'flint glass'; this glass has a very high lustre and can be readily worked, and so it is used for making 'cut glass' vessels. A form of flint glass, particularly rich in oxide of lead, sparkles brightly when cut so as to have suitable facets; hence it is used for making artificial, or 'paste', gems. If potassium carbonate, limestone and silica are fused together by heat then there results the so-called 'Bohemian' glass, which is difficult to melt and consequently is found useful for chemical and other work in which high temperatures are used. The silica portion of glass can frequently be partly replaced by boric oxide and in this way there are produced the 'borosilicate' glasses which have very important properties; certain glasses of this type are used for making optical lenses whilst a borosilicate glass containing sodium and aluminium, as well as traces of other metals, has been developed in the United States in recent years for making baking dishes and laboratory ware. This is known commercially as 'pyrex' glass, and its peculiar property is that, unlike most glasses, it can withstand sudden changes of temperature without cracking; baking dishes can thus be made quite thick and mechanically strong and yet they will withstand the temperature of an oven. The use of pyrex dishes, since they allow of greater cleanliness, is spreading in this country.

On reviewing the properties of the different glasses already described, it is seen that slight changes in the composition

of a glass will produce quite new characteristics ; although the subject is very complex a study has been made of the changes in various properties resulting from variations in the composition so that at the present time it is possible, to a great extent, to foretell the properties of a glass from a knowledge of the materials and methods used in its manufacture. In the same way it is often possible to calculate in advance the amounts of different constituents required to make a glass having certain particular properties.

If a coloured glass is desired for stained glass windows, or for the manufacture of table glass, then small amounts of various oxides are usually incorporated into the mixture of molten silicates during the process of manufacture. It has already been mentioned that oxide of iron produces a greenish colour ; cobalt oxide gives an intense blue and chromium oxide a green or greenish-yellow glass. Uranium produces a peculiar glass with a greenish-yellow fluorescence which can be made into attractive drinking glasses. The so-called 'ruby glass' contains metallic gold in an extremely finely divided form as the colouring material ; when the glass happens to be of the 'paste' variety then imitation rubies result. It should be made clear that these imitation rubies are quite different from artificial rubies, for the latter are identical chemically with the real rubies although they are made by man in his laboratory and not by Nature. By heating together aluminium oxide and chromium oxide in suitable proportions at a very high temperature artificial rubies may be obtained which are almost identical in every respect with the natural ruby ; the imitation gems made from glass are quite different chemically and also are much softer than the true ruby. Imitation 'paste' sapphires can also be made, but these again are quite different from the artificial sapphires which are chemically identical with the real gems.

Since the development of the sodium carbonate industry was due in the first place to its importance in the manufacture of soap, it will be appropriate to discuss the subject of soap at this point. Although the word soap (or sope) is mentioned several times in the Bible, it is very doubtful if the ancient Hebrews knew any substance which was at all related to the soap of to-day. It is probable that we owe to the Gauls the first discoveries which have led up to the development of an important accessory to health and cleanliness ; the Gauls

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prepared an impure soap by heating together beech-wood ashes, which contained potassium carbonate, water and goat's fat; the resulting product was used as a hairwash and for medicinal purposes. The Romans appear to have developed soap manufacture for washing purposes to a considerable extent; in the excavations at Pompeii, which was destroyed in A.D. 79, a complete soap-factory with utensils and materials was discovered.

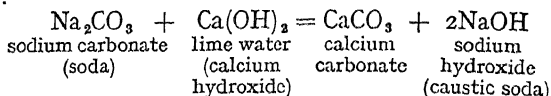
In England the manufacture of soap was started about the fourteenth century, and during the eighteenth century nine soap firms were established in London; the method used was to boil up any fat with a solution of alkali. The process of making soap at that time was empirical and the result of chance observations; it was known that the use of soda, or barilla, instead of potash, would generally yield a hard soap instead of a soft one, and that the addition of lime to the soda would yield a liquor (or lye) which was much more effective than the soda alone for converting the fat into soap, but the reasons were not clear. It was not till Chevreul, a Frenchman, published his important work on the chemistry of fats, between the years 1811 and 1823, that the manufacture of soap really became the science which it is to-day. We now know that all animal fats and vegetable oils are compounds of glycerine and certain acids known as fatty acids, chief amongst which are oleic acid (from olive oil), palmitic acid (from palm oil), and stearic acid (from ox or sheep fat); as a general rule most fats are mixtures of glycerine compounds of several fatty acids, but frequently one of these predominates. In the manufacture of soap the essential process is the splitting up or 'hydrolysis' of the fat by means of water, thus:

Fat and Water  $\rightarrow$  Fatty Acid and Glycerine.

This decomposition does not occur readily with water alone, but it can be considerably accelerated by the use of superheated steam or a hot solution of acid; the usual method is to use an alkali as the hydrolyzing agent and the resulting fatty acid neutralizes this alkali to form a salt; the process is called 'saponification'. The alkali salts of fatty acids are the substances which we call 'soaps'; the sodium salts generally form hard soaps whilst the potassium salts are the soft soaps, although the nature of the fatty acid also has some influence on the hardness of the soap. In the earliest days



of soap manufacture potash or soda, which are very mild alkalies, were used in the hydrolysis process, but the action was very slow and it was later discovered, as mentioned above, that the addition of lime was very beneficial. The lime converts the mild carbonate alkali into a strong caustic alkali, thus :



The resulting clear liquor, therefore, contains sodium hydroxide, which is often known as caustic soda. This is a very efficient agent for saponifying fats ; it is the one generally used at the present time, but it is now made to a great extent by another method involving the electrolysis of brine. The general process for the manufacture of soap in use to-day is to place a mixture of molten fat or oil and a solution of caustic soda in a large pan which is capable of holding up to half a million or more pounds of soap ; the mixture is heated by steam coils and also by blowing steam into the liquid. After some time, when the saponification process is complete, a strong solution of common salt is added and this has the effect of coagulating the soap ; on standing the solid rises to the top and forms a thick layer. The clear liquid below, which contains chiefly water and glycerine and some unused caustic soda, is first run off, and then the soap is removed ; after some purification it is run into moulds to cool and harden. Cheap soaps usually contain rosin compounds or sodium silicate which have been incorporated during manufacture, whilst perfumes are added for the production of toilet soaps.

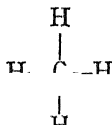
Glycerine, an important commercial article both for medicinal use and in the production of explosives, is generally recovered from the clear liquid which is run off during the manufacture of soap. This liquid is concentrated by evaporation under reduced pressure ; the process is continued until the residue contains about 80 per cent. of glycerine. The crude material is then subjected to 'steam distillation', that is, steam is blown through the liquid and the vapour coming off is condensed ; a solution of pure glycerine is obtained and it is concentrated further by evaporation. In general 100 pounds of any of the ordinary fats will yield 10

pounds of pure neutral glycerine after the above treatment, and the sale of this commodity has helped to reduce the cost of soap.

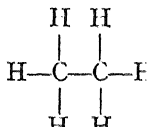
Before concluding this chapter an important group of carbon compounds must be mentioned; these are the compounds with hydrogen known under the general name of 'hydrocarbons'. Several hundreds of these substances have been recognized and many of them occur in Nature in the form of various kind of petroleum. Some hydrocarbons are gases, like 'marsh gas', others are liquid, like benzene and turpentine, whilst others, like rubber, naphthalene and paraffin wax are solids, but they all have one characteristic in common—they are inflammable and burn in air to form carbon dioxide and water. In order to simplify the study of these compounds the chemist has found it convenient to divide them up into a number of different groups or classes according to their chemical structures.

The first group to be considered is known as the 'paraffin' series; the word 'paraffin' is derived from two Latin words which mean 'little affinity', and this name is applied to these particular hydrocarbons because they are not easily acted upon by chemical reagents. The first and simplest member of the paraffin series is the gas called 'methane', or 'marsh gas'. This substance is produced during the decomposition of vegetable matter under water, and so when the bottom of a marshy pool is stirred bubbles of methane rise to the surface. The 'will-of-the-wisp', which is sometimes observed in marshy places, is probably due to these bubbles of gas liberated at different points suddenly catching fire, and hence the impression is obtained of a light dancing from place to place. Various natural gases originating underground, as, for example, at Heathfield in Sussex, and in various parts of Europe and America, as well as the 'casing-head' gas obtained from petroleum oil (p. 185), contain methane. Coal measures usually contain some of this gas which has accumulated during the formation of the coal from vegetable matter and it is set free during mining operations; the gas is, therefore, often found in coal-mines and forms the dread 'fire-damp' which is liable to form an explosive mixture with air. Coal gas, made by the carbonization of coal, contains about one-third or more of methane and this is greatly responsible for the heating power of the gas. Pure methane

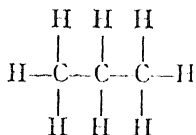
can be made in the laboratory, and it is found to be a colourless, odourless and non-poisonous gas which can burn readily; with air it forms a mixture which explodes on the application of a flame or spark. The chemical formula of methane is  $\text{CH}_4$  and since the valency (p. 24) of carbon is four and that of hydrogen is one, the structural formula is represented by



The next compound in the paraffin series is known as 'ethane'; it is also a gas and has the formula  $\text{C}_2\text{H}_6$  which may be written

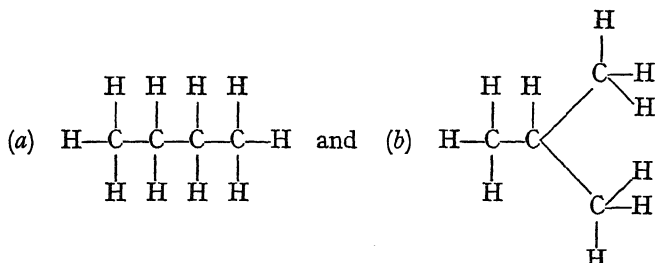


It should be noted that the difference between ethane ( $\text{C}_2\text{H}_6$ ) and methane ( $\text{CH}_4$ ) is a matter of one atom of carbon and two atoms of hydrogen, that is they differ by ' $\text{CH}_2$ ' and the same difference is always found between any two successive compounds of any series of hydrocarbons or other compound of carbon. The next member of the present series is, therefore,  $\text{C}_3\text{H}_8$  and this is known as propane; its structure is represented by the formula:



Following this comes  $\text{C}_4\text{H}_{10}$ , which can have two different chemical structures, thus:

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and each of these represents a perfectly distinct substance. The former is called normal-butane and has a straight chain of carbon atoms, whilst the latter is known as iso-butane and has a branched chain; both forms are found in petroleum. After butane we have  $\text{C}_5\text{H}_{12}$ , pentane, of which the three forms theoretically possible are known, whilst the next member of the series  $\text{C}_6\text{H}_{14}$ , hexane, exists in five forms. As the number of carbon atoms in the hydrocarbon increases, the possibility of the formation of branched chains also increases very rapidly, so that of the substance  $\text{C}_{13}\text{H}_{28}$  over 800 forms are theoretically possible! All have exactly the same *net* formula, but the atoms are built up in a different way in every case and a different substance results. The paraffin hydrocarbons  $\text{C}_{27}\text{H}_{56}$  and  $\text{C}_{31}\text{H}_{64}$  have been found in beeswax, and each of them must exist theoretically in thousands of different structural forms. We begin to see now why such a large number of hydrocarbons can exist even for one series only and there are several other series of importance.

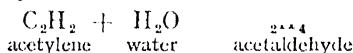
The next series to be considered are the 'olefines', of which ethylene is the first member; its formula is  $\text{C}_2\text{H}_4$  and its

structure is represented by 
$$\begin{array}{c}
 \text{H} \quad \text{H} \\
 | \quad | \\
 \text{H}-\text{C}=\text{C}-\text{H}
 \end{array}$$
 Ethylene is

made by heating ethyl (i.e. ordinary) alcohol with either concentrated sulphuric or phosphoric acid; it is a colourless, inflammable gas, forming an explosive mixture with air. It has been used in recent years as an anæsthetic, and also for producing the colour of ripeness on citrus fruit which, for purposes of convenience, has been picked when still green; it is also used to some extent in the blow-pipe, with oxygen, for cutting and welding metals. The next member of the olefine series is  $\text{C}_3\text{H}_6$ , and this is followed in regular steps by a number of other hydrocarbons up to, at least,  $\text{C}_{30}\text{H}_{60}$  which

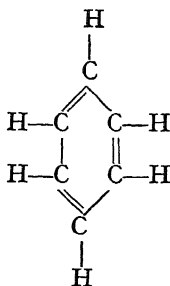
occurs in various waxes. Here again the power of forming straight and branched chains of carbon atoms results in the possibility of many thousands of different substances all having the same net number of carbon and hydrogen atoms united, however, in different ways.

The hydrocarbons of the third important series are called the 'acetylenes'; and, as the name implies, ordinary acetylene is the simplest member. This gas has the formula  $C_2H_2$ , that is  $H-C\equiv C-H$ , and it is generally prepared by the action of water on calcium carbide. The latter is made commercially by heating together lime and coal to a very high temperature in the electric furnace, and when water is dropped on the resulting carbide an impure form of acetylene with an unpleasant odour is produced; the pure gas has, however, only a faint odour. Acetylene burns readily, but produces a smoky flame; if a special jet is used then it can burn with a white highly luminous flame. A mixture of acetylene with air or oxygen is very explosive, but by means of a suitable burner a mixture of acetylene and oxygen may be burnt to produce a very hot flame (p. 51). Acetylene is used for lighting purposes in many places where coal gas and electricity are not available; for this purpose, as well as for the oxy-acetylene burner, it is generally dissolved under pressure in acetone which is absorbed in some porous material, and stored and transported in iron cylinders. Ordinary acetylene if stored under pressure is very liable to explode, and hence it is never transported in this way. Another danger in connexion with the use of acetylene is that it is liable to form explosive compounds when brought into contact with any material containing copper, as for example brass pipes and taps, and so great precautions must be observed when using this, otherwise valuable, gas. In recent years acetylene has played a vital part in the intermediate stage of an important technical process for the manufacture of acetic acid, which is used to a great extent in the manufacture of a certain form of artificial silk (p. 242). Acetylene gas is passed into water in the presence of a mercury salt or some other substance which behaves as a catalyst (p. 155), that is it stimulates the reaction without itself being affected by it, and a compound called acetaldehyde results.

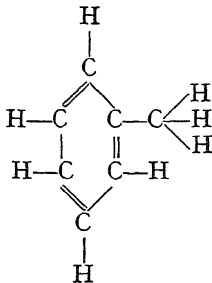


From acetaldehyde it is possible, by oxidation, to obtain acetic acid very readily, and this process of manufacturing the acid is carried out to a considerable extent at Shawinigan Falls, Canada, where cheap electricity from water power is used for making the calcium carbide required for the preparation of acetylene. Various members of the acetylene series up to  $C_{20}H_{38}$  are known, but they are not very important, neither do they occur in Nature.

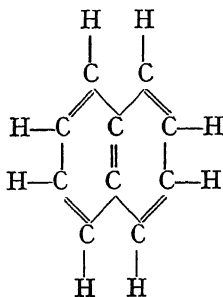
Although many other groups of hydrocarbons are known, only one more, namely the benzene series, will be considered here. The members of this group differ fundamentally from those of the other series which we have already considered, in one important respect; whilst the carbon atoms in the previous series are arranged in chains, either straight or branched, in the benzene series six carbon atoms form a closed ring. Thus the formula of benzene itself,  $C_6H_6$ , is generally written:



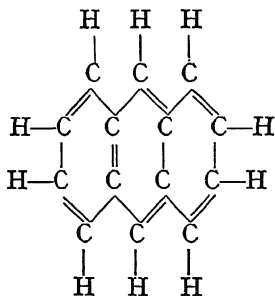
and this six-carbon ring is generally called the benzene ring. Additional members of the series result, as with the other groups of hydrocarbons, when the formula is increased by  $CH_2$ ; thus toluene is  $C_7H_8$ , and may be written:



The next member of the series,  $C_8H_{10}$ , can exist in four different forms. Three of these are known as xylenes whilst the fourth is called ethyl benzene. As the hydrocarbons become more complex naturally many different forms, all having the same formula, can and often do exist. Benzene, toluene and the xylenes are all obtained from coal-tar and they are the parent substances for many important industries (p. 194). Closely related to the benzene series of hydrocarbons is the naphthalene series; naphthalene itself, commonly known in the form of 'moth-balls', is the simplest member of the group and the molecule may be regarded as made up of two benzene rings joined together, thus :



The anthracene series is based on the addition of a third benzene ring, thus :



These and other, even more complex, hydrocarbons are obtained from coal tar.

This brief review will serve to indicate that a large number

of hydrocarbons can exist and there will be occasion to refer to some of them from time to time in subsequent portions of this book.

## QUESTIONS

1. How are (a) water glass and (b) caustic soda prepared? For what purposes are they used?
2. Give a brief outline of the chemistry of soap manufacture.
3. How is glycerine obtained?
4. Name the more important groups of hydrocarbons; mention one example in each group.

## SUBJECTS FOR ESSAYS AND DISCUSSIONS

1. The history of glass and its influence on civilization.
2. The history of soap and its influence on health.
3. Chemistry in the glass industry.
4. Hydrocarbons.

## FURTHER STUDY

1. The manufacture of glass and soap.
2. Artificial and imitation gems.
3. Ceramics.
4. The chemistry of hydrocarbons.

## BOOKS TO READ

Chemistry in Modern Life. Arrhenius. (Chapman & Hall.)  
Chemistry in the World's Work. Howe. (Chapman & Hall.)  
Chemistry in the Service of Man. Findlay. (Longmans, Green.)  
Chemistry Applied to Home and Community. Beery. (Lippincott.)  
Chemistry in Industry. Vol. II. (Chemical Foundation, New York.)

An elementary text-book of Organic Chemistry.

## SUGGESTIONS FOR EXPERIMENTS

Preparation of soap from fat.  
Preparation of caustic soda from washing soda.  
Preparation and properties of methane, ethylene and acetylene.  
Examination of benzene, naphthalene and anthracene.  
Water glass: properties and uses.



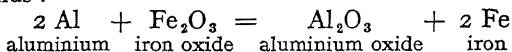
## CHAPTER VIII

### BURNING AND BREATHING

THE old adage says 'fire is a good servant but a bad master', and the ability to conserve and control fire has been a very great factor in man's social and cultural development. Primitive man realized the benefits which fire could bring to him, but at the same time he knew of its terrors, and so he looked on fire with awe and veneration; thus the worship of a Fire God became general in many parts of the world. In later times the mystery of fire and its origin stimulated the development of legends, and these were handed down from one generation to another and accepted as the truth. Thus according to the ancient Greeks fire was first brought to the earth by Prometheus, who stole it from Heaven and showed mankind how to use it to their advantage, whilst other nations have other mythological accounts of the origin of fire. Whether man first learned to control natural fires, for example those caused by volcanoes, lightning and meteorites, or whether he learned first to make his own fires by friction or by striking flints, it is impossible to say, but probably the small fires made by artificial methods would have been more easily controlled. Even in recent times primitive peoples living on the islands of the Southern Pacific have been found using the same methods that were probably used in the first man-made fire. To-day, although we can still only conjecture as to how fire was first kindled on the earth, yet thanks to the work of chemists, the nature of fire is no longer the intense mystery that it was only a few hundred years ago.

When two or more substances react together chemically and entirely new products result—in other words, when a chemical change occurs—there is generally, although not always, a liberation of heat. Sometimes the quantity of heat produced is so great that the materials involved are made

red or even white hot ; we have a very striking example of this fact in a reaction of technical importance. If aluminium powder is mixed with oxide of iron and a chemical action started by means of a suitable fuse, then the aluminium takes up the oxygen from the oxide of iron and leaves metallic iron, thus :



During the course of this action a very considerable amount of heat is liberated, and this is sufficient to cause the iron, which results in the process, to melt ; the molten iron may be used for joining together two pieces of the metal. This reaction forms the basis of the 'thermit' process used for welding together tram rails, and for joining up breaks in the ironwork of locomotives and ships. The 'thermit' mixture was actually used in some of the incendiary bombs dropped by aircraft in the early days of the last war. In this particular reaction the substances taking part in, and resulting from, the process are all tangible and visible, and we have no doubt that the heat evolved is due to the chemical change which occurs ; in most cases of heat production, however, one of the substances entering into the process is the invisible gas oxygen and hence, as we shall see later, the explanation of the phenomenon of burning proved a difficult matter.

In general we now use the term 'combustion' or 'burning' to describe chemical changes which are accompanied by the production of heat and light. Such common processes of daily life as the burning of coal, gas or wood—in fact any of the methods, except the electrical ones, used for the production of heat and light—involve chemical changes and are instances of combustion. The work of the French chemist Lavoisier in 1777, and also of other earlier and contemporary scientists, showed that the breathing of animals and human beings involved chemical processes very similar to those which occur during burning. In the latter case, however, the changes occur so quickly that the heat produced is sufficient to warm the resulting substances up to the temperature at which they catch fire ; in the body the changes occur slowly and the heat is only liberated gradually and so the temperature never rises very considerably. In the process of breathing, therefore, we have an example of *slow* combustion.

Cases are known in which the heat evolved, as the result

of a process of slow combustion, accumulates until the temperature is sufficient to allow rapid combustion to occur and the whole mass catches fire; we then say that *spontaneous* combustion has occurred, or that the material has set itself on fire. It is well known by farmers that if hay is stacked in a damp condition it is liable to catch fire spontaneously; this is due to the fact that chemical changes go on in the damp hay and these changes are accompanied by the liberation of heat. This heat accumulates in the interior of the stack and the temperature increases gradually until eventually the hay is raised to its burning or ignition point and so catches fire. Coal has been known to catch fire spontaneously when stored in bunkers, because some of the coal dust is slowly acted upon by the oxygen of the air and heat is produced; if the coal is in an open place the heat can be dissipated and the temperature does not rise, but if the heat cannot escape it will accumulate, and eventually the temperature of the coal will be raised to the point at which it reacts rapidly with oxygen and a fire results. Oily rags, cotton bales and decomposing animal matter have been known to catch fire spontaneously for similar reasons.

It is important to note that fire does not always mean flame; a piece of charcoal when burnt will glow red hot, and although it gives out a considerable amount of heat there is almost no flame; wood or coal on the other hand produce flames readily. The explanation is that flame only results when a gas or vapour is raised to a high temperature as the result of a combustion process; without gas or vapour of some kind flame is impossible. When coal or wood are heated vapours are given out in considerable quantities and so flames can be produced; charcoal, on the other hand, is the residue from wood after nearly all the vapours have been driven off and hence this can produce very little flame on burning. Gases, and easily volatile liquids like benzene, petrol and paraffin, which yield vapours very readily, naturally produce flames when they burn. Before flame results, however, it is essential that the temperature of the gas or vapour should reach a certain point called the 'ignition temperature', which varies with the nature of the inflammable gas.

In their attempts to solve the problem of the constitution of matter the old Greek philosophers regarded fire as an element which existed in all substances able to burn, whilst,

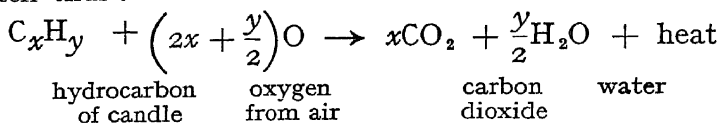
at a later date, the alchemists thought that a 'fire principle', exemplified by sulphur, was always present in inflammable materials. Even Robert Boyle, who gave us our modern conception of an element (p. 8), thought that fire could be weighed in a balance and hence was something material. The first semi-scientific attempt to explain combustion, or burning, was made by a German chemist named Becher and his pupil Stahl during the seventeenth century. They considered that everything contained to some extent a mysterious substance called 'phlogiston' (from a Greek word which means 'to inflame'); as a result of burning or heating the phlogiston was said to be liberated. It had been known for some time that when a metal is heated very strongly in the air it produces a calx or ash, and it was considered that this calx represented the metal which had lost its phlogiston, thus:

Metal = Calx + Phlogiston (escapes).

It was found, however, that the calx, in spite of having *lost* phlogiston, had actually *gained* in weight, and hence it could only be concluded that the phlogiston weighed less than nothing! This certainly strikes us as quite absurd at the present time, but apparently it did not seem such a very remarkable thing as recently as 150 years ago! Towards the end of the eighteenth century Lavoisier showed by a series of careful experiments, some of which have already been described (p. 42), that a metal gains in weight when it is heated because it takes up one of the constituents of the air, namely oxygen. He proved, too, that all the common processes of burning, and also of breathing, involved the utilization of the oxygen of the air, and that in every case the heat liberated was due to a chemical reaction between the combustible substance and oxygen. All the observed facts could be readily explained in this way without making any assumptions concerning a mysterious phlogiston. The oxygen theory of burning was thus founded, and although it met with a great deal of opposition at the time of its introduction, even from such able scientists as Priestley and Cavendish to whose work frequent reference has already been made, yet it is the accepted explanation at the present day.

We have a simple example of the application of the theory in connexion with the burning of a candle; the material of the latter, consisting mainly of hydrocarbons, is turned into

a vapour which unites chemically with the oxygen of the air. The carbon forms carbon dioxide, which can be detected by means of lime water (p. 78), whilst the hydrogen forms water vapour, the presence of which can be shown by the formation of drops of water on a cold surface placed just above the candle flame. As a result of this chemical reaction enough heat is liberated to raise the hydrocarbon vapour, rising from the wick, to a temperature above its ignition point and so a flame is produced. The reaction may be written thus :



Pure oxygen will naturally stimulate burning to a much greater extent than does air which contains only one-fifth part of oxygen; hence we have some of the important uses of this gas already mentioned (p. 50). In the absence of air, or oxygen, a fire will not continue to burn, and this knowledge is utilized when flames are smothered by means of a blanket. Fire extinguishers (p. 76) are generally small generators of carbon dioxide gas; this is a heavy and non-inflammable gas, and so acts as a blanket and keeps the air away from the fire. In recent years the so-called 'fire-foam' extinguishers have been developed to deal chiefly with oil fires; these extinguishers produce a thick foam containing bubbles of carbon dioxide gas and this smothers the fire and prevents it from spreading. Firefoam chemicals are generally made in two parts: one consists of aluminium sulphate, or alum, and the other of sodium bicarbonate and a foaming agent like glue, glucose, licorice extract or saponin; on mixing the two solutions the carbon dioxide foam results. 'Pyrene' extinguishers contain a liquid called carbon tetrachloride which forms a heavy non-inflammable vapour; this also prevents access of air to the fire and so smothers it. On the other hand, if we want to stimulate a fire to burn, as in a grate, for example, we encourage the air to get to the fire, either by blowing with a bellows, or else by covering up the chimney opening so that all the air-draught passes through the grate.

Burning can take place under water provided that the necessary amount of oxygen is supplied; this can be done

in several ways. Gunpowder, for example, can, by suitable means, be set on fire and will continue to burn under water ; this happens because the potassium nitrate, sometimes called nitre or saltpetre, contained in the powder can supply the necessary oxygen for the combustion of the carbon and sulphur, the other constituents of the mixture. If oil is forced into water by means of compressed air it is possible to set it on fire and obtain a very hot flame burning under water. This idea is being developed commercially in the Brunler flame ; the great value of this flame is that the heat can be transferred directly to the water without having to pass through any intervening material such as a boiler. It is possible that there may be important developments in the near future of this economical method of steam raising.

Although most substances require oxygen in some form in order to burn, there are a few cases known in which burning can occur in its complete absence ; for example, a thin sheet of copper can burn in the vapour of sulphur or in chlorine gas, whilst phosphorus and arsenic will inflame if dropped into liquid bromine. In each case a vigorous chemical action occurs and the quantity of heat liberated is sufficient to cause the production of flame. We can thus see that, in general, fire is not a mysterious material element, as the ancients considered it to be, but simply the manifestation of the heat energy which is liberated when a chemical change occurs.

The similarity between breathing and burning has already been mentioned from time to time and hence it would not be out of place to examine here in some detail the respiration processes of various living organisms. We shall see later that in the case of human beings and animals, food material, consisting of carbon compounds, is stored up in various muscles of the body and there combines with oxygen ; as a result of the chemical action heat for maintaining the body temperature is liberated, and energy is supplied for doing work. The oxygen essential for this process of slow combustion is supplied from the lungs and carried to the various muscles by means of the blood which is continually circulating round the body. Oxygen is only slightly soluble in water and in blood, which is mainly water, and if the body were compelled to rely only on the oxygen which the blood could dissolve there would have to be a very much more vigorous circulation ; the heart would then have to work far more rapidly than under normal

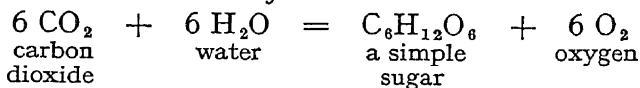
conditions. Fortunately Nature has devised another way of carrying oxygen round the body.

In human blood there are present a large number of red cells or corpuscles; these contain a complex chemical substance, consisting of carbon, hydrogen, oxygen, nitrogen, iron and possibly sulphur, known as hæmoglobin. This substance has the power of forming a loose chemical compound with oxygen called oxy-hæmoglobin; it has a bright scarlet colour characteristic of arterial blood, whilst the hæmoglobin itself is dark red. As the corpuscles pass along the capillaries of the lungs the hæmoglobin unites with the oxygen from the air which has been breathed in, and the scarlet arterial blood, now charged with oxygen to a much greater extent than solubility alone would permit, passes into the heart and is pumped round the body. At various muscles the oxy-hæmoglobin gives up its oxygen and this unites with the carbon and hydrogen of the food material to form carbon dioxide and water; these enter the blood stream which is now dark red in colour, due to the hæmoglobin, and is known as venous blood. When the lungs are reached again the carbon dioxide, together with all the nitrogen of the original air and the unused oxygen, are discharged when breathing out, whilst the hæmoglobin is re-oxidized and passes on again to perform its function as oxygen carrier. Ordinary air before inhalation contains approximately 79 per cent. of nitrogen, 20.96 per cent. of oxygen and 0.04 per cent. of carbon dioxide, whilst exhaled air contains about 80 per cent. of nitrogen, 16 per cent. of oxygen and 4 per cent. of carbon dioxide. The presence of the latter gas in considerable amounts is easily shown by breathing into a vessel containing lime water (p. 78); a milkiness due to the formation of calcium carbonate is readily produced.

In the breathing of animals and human beings, and of fish and insects too, oxygen is continually being used up and replaced by carbon dioxide, yet the amount of the latter gas in the air hardly varies from three or four parts in 10,000 volumes of air; evidently some process is at work which reconverts the carbon dioxide into oxygen and so helps to maintain a balance, or equilibrium. The clue to the nature of this process was obtained by Joseph Priestley during the course of his experiments on air. Whilst attempting, by various means, to restore to its original condition air which

had been vitiated by the burning of a candle, or the breathing of animals, he made a very important discovery. 'On the 17th of August, 1771', says Priestley, 'I put a sprig of mint into a quantity of air in which a wax candle had burned out and found that on the 27th of the same month another candle burned perfectly well in it. This experiment I repeated not less than eight or ten times in the remainder of the summer. This remarkable effect does not depend on anything peculiar to mint', he continues, '. . . for on the 16th of July, 1772, I found a quantity of this kind of air (that is, vitiated air) to be perfectly restored by sprigs of balm which had grown in it.' Priestley proved that the smell of the plant had nothing to do with the restoration of the air, for he says that he obtained 'equally complete restoration of this vitiated air by the plant called groundsel which is usually ranked amongst weeds and has an offensive smell'. Priestley also showed that plants could revive in the same way air which had been vitiated by the breathing of animals. Evidently plants can take up carbon dioxide present in the vitiated air and give out oxygen which is required for burning to occur. Later investigation showed that this process goes on in the green parts of plants only, and even there only in the presence of sunlight; under these conditions carbon dioxide and moisture can be built up into carbohydrates, such as starches and sugars (p. 128), and oxygen set free.

This process is known as 'photosynthesis', which means building up in the presence of light, and the first stage of the reaction which occurs may be written:



In the next stage two or more molecules of the simple sugar may unite to form a complex sugar, or starch, or cellulose (p. 128). The sugar, or starch, contains much more energy than do the carbon dioxide and water together; this energy is derived from sunlight and can be made available for doing work by slow combustion of sugar or starchy food in the living organism. In this way almost all human energy comes ultimately from the sun. The green parts of plants in which the process of photosynthesis occurs are very tiny bodies known as 'chloroplasts'; these are about one five-thousandth part of an inch in diameter, but there are enormous numbers



present in every plant. Thus it has been calculated that the chloroplasts in a well-grown castor-oil plant have a total surface area of about one acre! The sunlight falling on such a plant is, therefore, given every opportunity to be absorbed, and although only a very small proportion of the total light falling on each chloroplast is actually used the total amount of photosynthesis is quite considerable. These chloroplasts contain a green colouring matter generally known as 'chlorophyll', although careful analysis has

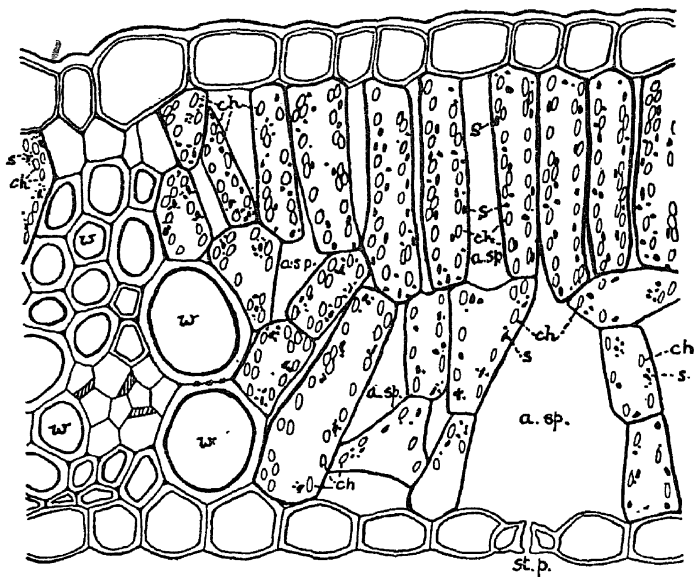


FIG. 12.—Transverse Section (magnified) of a Green Leaf

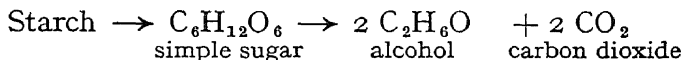
Air containing carbon dioxide enters through the stomatal pore (*st. p.*) and circulates in the air space (*a. sp.*); water is brought from the soil by the woody tissues (*w.*). Energy is absorbed from sunlight by the large number of chloroplasts (*ch.*) and starch granules (*s.*) are formed.

shown it to consist probably of four different substances; the most important of these are known as chlorophylls A and B and they are apparently related to the hæmoglobin of the blood except that they contain magnesium instead of iron. Chlorophyll is the essential factor in plant photosynthesis; in its absence carbohydrates cannot be built up and oxygen cannot be set free. We thus see that green plants play a very important part in keeping the air pure and maintaining the equilibrium between oxygen and carbon dioxide.

The carbon dioxide cycle, as it is often called, is one of the most remarkable examples of the wonderful balance of Nature ; the waste product of animal life is the essential for vegetable life and vice versa.

It is important to remember that photosynthesis is not the only process similar to breathing which goes on in a plant ; it can be shown that at all times, both in the dark and in sunlight, plants breathe just as do human beings and animals. That is, they always take in oxygen and pass out carbon dioxide ; in sunlight, however, the reverse process of taking in carbon dioxide and sending out oxygen by the green parts of the plant, far outweighs the ordinary breathing. At night plants breathe like human beings, and hence they enter into competition with us for the available air. For this reason plants are generally removed from bedrooms at night, although, as a matter of fact, the amount of air used by a plant is so small that it would be unnoticeable in a reasonably well-ventilated room. It has been calculated that forty sunflower plants liberate no more carbon dioxide at night than would be produced by one man ! Nobody is likely to have so much vegetation in a room at night and hence the danger of plants vitiating the air of a bedroom is very small.

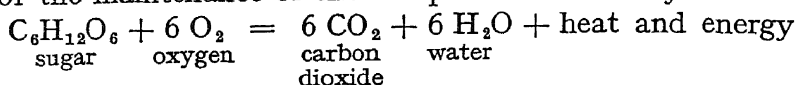
Since oxygen is essential for normal plant and animal life we may obtain the impression that all living organisms must have air for purposes of respiration ; this would, however, not be quite correct. Peas, and seeds generally, can develop and germinate to some extent even in the complete absence of air or oxygen ; during this process of germination the lime-water test shows that carbon dioxide is given off, and hence the material of the seed is being decomposed. Further examination has shown that alcohol is produced at the same time, and that both this and the carbon dioxide result from the decomposition of a simple sugar produced by starch (p. 129) stored in the seed, thus :



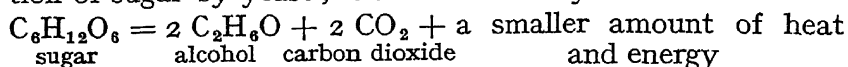
If the store of starch in the seed is exhausted and the normal life requirements of a plant—air, carbon dioxide and sunlight, at least—are not supplied, life will soon become extinct.

Certain very simple forms of vegetable life, such as the yeasts for example, can live and reproduce quite normally either in the absence of, or in the presence of, oxygen, as

long as food material, consisting mainly of sugar and water, together with traces of the elements nitrogen, phosphorus, calcium and magnesium, is supplied. In the presence of air the sugar is consumed in the ordinary way to form carbon dioxide and water and the energy liberated becomes available for the maintenance of the life processes of the yeast.



In the absence of air this reaction clearly cannot occur ; but as the organism must obtain its energy in some way, an alternative process occurs in which oxygen is not required. A smaller amount of energy is set free in this way, as a result of the decomposition of a given amount of sugar, than if oxygen were available. This alternative process produces carbon dioxide and alcohol and is the basis of the fermentation of sugar by yeast ; the reaction may be written :



It has been known for a very long time that if yeast is added to sweet dough, or to a sweet liquor, then the mixture froths up and gives the appearance of boiling ; for this reason the process was called 'fermentation', from a Latin word which means 'to boil'. The action which occurs in the interior of the dough, or under the surface of the liquid, is that the yeast in order to continue to live and reproduce itself is compelled, in the absence of oxygen, to decompose the sugar present into alcohol and carbon dioxide ; the evolution of the latter in the form of bubbles gives the impression of boiling. In the case of the leavening of dough the carbon dioxide gas forms a large number of small bubbles ; in the process of baking these bubbles expand and so they distend the dough and make it 'light' and porous. Since this process of leavening, as it is called, depends on the decomposition of sugar, it is essential that this substance should be added to the dough. In the fermentation of barley extract for the production of beer, or of fruit juices in the making of wine, it is chiefly the alcohol which is required ; the carbon dioxide in these cases is a by-product, but it is often collected and sold.

Yeast is an example of an 'anærobic' form of life, because it can exist in the absence of air, and there are many other

primitive organisms, such as bacteria, which can live under similar conditions. Not all of these, however, obtain their energy from the same source as does yeast; they frequently use different food materials and yield different products. In ordinary alcoholic fermentation other substances, in addition to alcohol and carbon dioxide, are formed to some extent and the nature and quantity of these depend on the organisms present. For this reason the fermentation industries have attempted to prepare cultures of pure yeasts of the most desirable type which can be used to make a perfectly uniform beer; if another yeast, or bacterium, should be introduced from the air, or in any other way, then the fermentation process will be somewhat different and the beer will not be of the same type. Special yeast cultures have also been developed which are regarded as most suitable for use in bread-making.

#### QUESTIONS

1. What is the relation between heat and chemical action? Illustrate with examples.
2. How did the discovery of oxygen enable burning to be explained?
3. Explain the terms slow combustion and spontaneous combustion.
4. Why does not flame always accompany burning?

#### SUBJECTS FOR ESSAYS AND DISCUSSION

1. The development of ideas concerning fire.
2. The extinction and stimulation of fires.
3. The part of oxygen in life processes.
4. The carbon dioxide cycle in Nature.

#### FURTHER STUDY

1. The avoidance of spontaneous combustion in the storage of coal, hay and cotton.
2. The struggle between the phlogiston and oxygen theories of combustion at the end of the eighteenth century.
3. Methods of making fire and light (matches, mantles, etc.).
4. Photosynthesis.

#### BOOKS TO READ.

The Chemistry of Combustion. Friend. (Gurney & Jackson.)  
The Chemical History of a Candle. Faraday. (Dent.)  
A History of Chemistry. Brown. (Churchill.)  
Chemistry in Modern Life. Arrhenius. (Chapman & Hall.)  
Chemistry in Agriculture. (Chemical Foundation, New York.)  
Chemistry in Industry. Vol. II. (Chemical Foundation.)

#### SUGGESTIONS FOR EXPERIMENTS

Test for carbon dioxide and water in exhaled air.  
Examination of gases produced when a candle burns.  
Breathing by plants in the dark and in sunlight.  
The action of yeast on a sugar solution.

## CHAPTER IX

### FLAME AND EXPLOSION

IN the previous chapter it was stated that a flame results when the gas produced in a combustion process is raised to a high temperature by the heat developed at the same time ; it would be interesting to look further into the structure of flame and to discover the cause of luminosity. If the flame of a candle is examined, it will be found to consist of a central non-luminous zone, above the wick, surrounded by a white luminous portion and finally a thin, almost invisible and non-luminous mantle, which is blue at the bottom, encircles the whole flame. The different parts of a candle flame have been explained in this way : the molten material of the candle is drawn up the wick and vaporized by the heat ; this vapour, we know, can only burn where it meets the air. In the non-luminous zone round the wick the vapour has not enough air in which to burn and so this portion of the flame consists of unburnt hydrocarbon vapours and really is not flame at all ! If a piece of string or a strip of wood, e.g., a match, is placed quickly into a candle flame and then withdrawn after a few seconds, it will be seen that the part which has been in the central non-luminous zone of the flame is almost untouched whilst the other parts are burnt. By placing the end of a thin glass tube into the centre of a candle flame it is possible to draw off the unburnt vapours and burn them at the other end of the tube about two or three inches away from the candle itself ! In the next zone of the flame, which is the luminous portion, combustion, that is oxidation, has commenced ; the process is finally completed in the outer non-luminous zone and this is incidentally the hottest region of the flame.

Over a hundred years ago, in 1816, Sir Humphry Davy attributed the luminosity of a flame to the presence of tiny unburnt particles of carbon raised to a white heat as a result

of partial burning; in fact, by putting a cold surface—a piece of broken china, for example—into the luminous part of a candle flame a black deposit of carbon can actually be obtained. Although the presence of incandescent, that is, white hot particles of carbon will partially explain luminosity, it cannot be accounted for completely in this way; we shall see that other factors are involved. In 1859 Frankland burnt some candles at Chamonix at the foot of Mont Blanc and some more of the same kind at the summit of that mountain; he noticed that although the candles burnt at the same

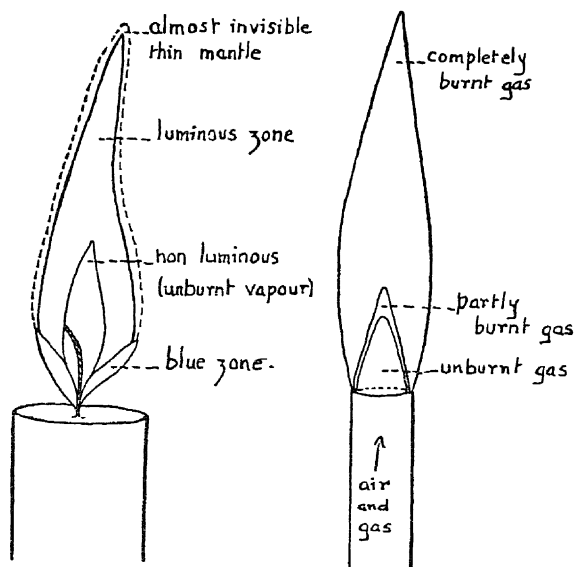


FIG. 13.—Candle Flame (left) and Air-gas, or Bunsen Flame (right)

rate in both places the luminosity on the summit, where the pressure of the air was, of course, low, was much less than at the lower level. Luminosity may, therefore, be connected in some way with the presence of unburnt gases at high pressure; a reduction of the atmospheric pressure, such as occurs at high altitudes, will result in a decreased illuminating power. It is interesting to note in this connexion that hydrogen gas under ordinary pressures burns with a non-luminous flame, but under increased pressure the flame is luminous although it contains no solid particles to become incandescent.

The luminous coal-gas flame which was so widely used for lighting purposes before the invention of the gas mantle has a structure which is very similar to that of the candle flame, although the shape is different. In order to increase the illuminating power of gas complex hydrocarbons were often added, and these decomposed in the flame and produced particles of carbon which could be raised to incandescence. At the present time, this addition is unnecessary, since illuminating power is not essential.

If coal-gas is mixed with air before being burnt we obtain a non-luminous flame of quite a different type ; this flame is very much hotter than the luminous flame, and it is used in gas-cookers, gas-fires, for incandescent mantle burners and in all cases where a high temperature is the main consideration. The burner is so made that as the gas rushes through a jet it draws two or three times its own volume of air along with it through holes specially provided for the purpose ; since the gas is already mixed with air it can naturally burn more completely than otherwise. As a result there is very little partly burnt gas, or carbon, and so we get no luminosity, but a high temperature. The air-gas flame consists of three portions ; there is first a colourless or very pale blue inner zone of unburnt gas, then a thin more bluish region of partly burnt gas and finally an almost colourless, or pale purple, outer zone in which combustion is complete. The latter region is naturally the hottest part of the flame, and the temperature there may be over  $1,600^{\circ}\text{C}$ . ( $2,900^{\circ}\text{F}$ .).

If the amount of air mixed with the gas is decreased, by partly closing the air-holes, the nature of the flame gradually alters until it becomes identical with an ordinary luminous flame. By opening the air-holes further the amount of air admitted is increased, and again the flame alters its appearance ; the inner zone of unburnt gas naturally decreases in size, because more air is available for its combustion. The flame becomes hotter, too, and starts to make a roaring noise. If the proportion of air to gas exceeds a certain amount then the flame ' strikes back ' and lights at the small jet through which the gas alone is coming ; a luminous flame is produced in which only partial combustion occurs and various gases, chiefly acetylene derivatives, are formed which have the characteristic unpleasant smell of a flame which has ' struck back '.

By heating various salts in the air-gas, or Bunsen burner, as it is known to the chemist, it is possible to obtain flames of different colours; sodium salts give an intense yellow, potassium salts a violet, barium a green, and strontium a crimson flame. This knowledge is frequently utilized in the production of coloured flares and fireworks.

It has been mentioned (p. 96) that a gas inflames when its temperature reaches a certain 'ignition' point; this fact was discovered by Sir Humphry Davy in 1815 during the course of his investigations on the cause and possible prevention of fire-damp explosions in coal-mines. He found that below a certain temperature methane, that is 'fire-damp', will not burn or explode when mixed with air, and this discovery led him on to invent the famous Davy lamp for use in mines. This lamp has undoubtedly resulted in the saving of many lives and for a long period it was universally used; it is being replaced to some extent at the present time, however, by electric lamps. The principle of the Davy lamp can be made clear by reference to a simple experiment; if a piece of wire gauze is brought down over a flame, then it will be observed that the flame continues to burn on the underside of the gauze only. Although the gas itself passes through the wire gauze it does not inflame above it, unless a light is brought directly to the gas. This failure of the gas to burn above the gauze, although it is alight below, is due to the fact that the wire gauze conducts the heat of the flame away so rapidly that the gas above does not reach

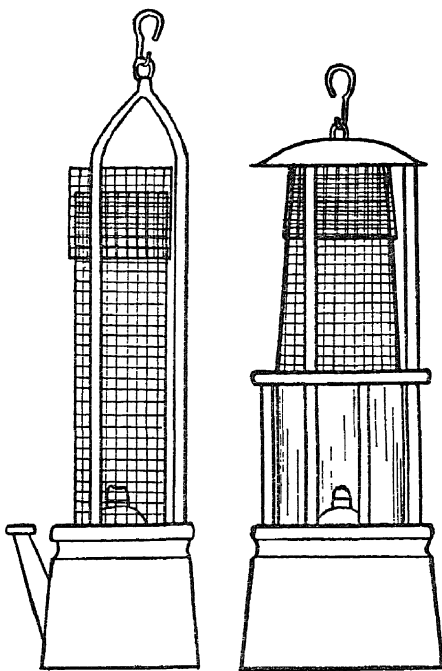


FIG. 14.—Davy Safety Lamps  
Old pattern (left) and newer pattern (right)



the ignition temperature. In the safety lamp, Davy surrounded a small oil lamp completely by a cylinder of wire-gauze closed at the top by a double layer of the same material. When placed in an atmosphere of inflammable gas the latter passes through the gauze and can inflame *inside* the lamp, but owing to the cooling effect of the gauze the gas outside cannot be ignited. The presence of methane in mine air can generally be detected by the production of a 'cap' above the ordinary lamp flame due to the burning of this inflammable gas; the amount of fire-damp present can, in fact, be roughly estimated from the size of the cap. If the gauze should become specially hot at one point or if the Davy lamp is exposed to a strong current of air, say a draught, the flame is liable to be driven through the gauze and so may cause ignition of the fire-damp outside; in order to avoid these dangers the lamp has been modified, and the newer form incidentally gives a better illumination. The lamp is surrounded by a strong glass cylinder, which allows the light to pass through better than the gauze, and the gauze cylinder is fixed to the top of this; there is thus no risk of overheating or of the flame being blown through.

When a chemical process in which gases are produced takes place with great rapidity we get a sudden flash of flame and an explosion; substances in the vicinity of, and surrounding the reacting materials are shattered with great violence and noise. The name 'explosive' is given to those substances which can be transformed, by appropriate treatment, almost instantaneously and completely into gases at high temperature. If the chemical transformation takes place very rapidly, then the heat of the reaction is evolved so quickly that a temperature of about  $4,000^{\circ}\text{C.}$  may be reached; if the process occurred slowly then a large proportion of the heat would be radiated away and such a high temperature would not be obtained. It is well known that the volume of a gas increases considerably as its temperature is raised, and so as the result of an explosive reaction very large volumes of gas are suddenly produced from a small quantity of explosive material. For example, when nitroglycerine, which is used in dynamite, explodes it produces nearly 20,000 times its own volume of gases. It can easily be realized that if such a tremendous amount of gas is suddenly set free in an enclosed space a huge pressure, amounting to hundreds of thousands of pounds

to the square inch, will be produced and a violent disruptive force will be exerted on the enclosing material.

An explosion may result from the interaction of different substances in a mixture, as in gunpowder, which is a mixture of nitre, carbon and sulphur, or ammonal, made from ammonium nitrate and aluminium, or else as the result of the disintegration or decomposition of an unstable material such as guncotton (nitrocellulose) or lyddite (picric acid). In a mixed explosive like gunpowder, the chemical action is usually slower than it is with a single substance, because in the former case the separate molecules of nitre, carbon and sulphur have to come together before the explosive chemical action can occur, whereas every molecule of the single substance can disintegrate independently of the others. When the explosive action takes place *comparatively* slowly we have a 'low' explosive (e.g., gunpowder) whilst such substances as lyddite, which disintegrate with great rapidity, are called 'high' explosives. Substances which explode with extreme rapidity and power are known as 'detonants' and the explosion is called a detonation; the best known detonant is mercury fulminate, which is used in percussion caps.

It is sometimes considered that explosives are only used for military purposes, but the error of this belief will be realized when it is known that nearly half-a-million tons of explosives are used per annum even in peace time. Explosives are used to a large extent in quarrying and in mining coal, iron ore and other important minerals. The construction of canals, tunnels, railways and roads requires various explosives in order that rocks and other obstacles may be broken down. In general different explosives are required for different purposes and some of these are of interest and worth further consideration. In a rifle or gun, it is necessary to have in the first place a propellant, or progressive explosive, which will drive the bullet out of the barrel; if a high explosive like lyddite or T.N.T. (tri-nitro-toluene) were used for the purpose, the rapidity of the explosion would probably burst the barrel of the gun, and so a low explosive must be used. For sporting guns 'black powder', that is, gunpowder, is generally used; for military purposes a special gelatinous form of gun-cotton is used or else a mixture of gun-cotton and nitro-glycerine, known as 'cordite'. The main body of the shell which is expelled from the gun contains a high

explosive, such as lyddite or T.N.T., so that a shattering effect may be exerted at the place where the shell falls. In mining and quarrying where large blocks of coal or stone are desirable a low explosive like gunpowder or ammonal is used, but if a shattering effect is required ordinary gun-cotton or dynamite will serve the purpose best. In the case of a low explosive it is necessary to confine the explosive material in an enclosed space or else much of the effect will be lost, but with a substance like dynamite the action is so rapid that the air is sufficient enclosing medium. It is stated that if a roll of dynamite is exploded in the open on a bridge the latter will be cut in two.

For use in coal-mining special 'safety' or 'permitted' explosives are required in order to eliminate the possibility of a fire-damp explosion. It may be mentioned, too, that finely divided coal dust suspended in air makes an explosive mixture and there have been a number of accidents attributable to such mixtures. The mixture of methane (fire-damp) and air present in a 'gassy' mine will only explode if it is heated locally to a certain temperature for a sufficient time, and hence the explosive mixture used in blasting should be required to burn fairly quickly and yet not produce too high a temperature, or too large a flame. These objectives are generally achieved by mixing a high explosive with an inert salt, like sodium chloride, magnesium sulphate, borax or ammonium oxalate, which acts as a cooling material and prevents too high a temperature being reached. Ammonium nitrate is used in a number of 'safety' explosives together with nitroglycerine, T.N.T. or some other high explosive. The problem of finding really satisfactory explosives for use in gassy mines is so important that an experimental station for investigating this and other subjects has been opened at Buxton by the Safety-in-Mines Research Board.

We have so far said nothing concerning the method of igniting or 'setting-off' the explosive. Gunpowder and gun-cotton may be set off by simple ignition with a spark from a fuse or by an electrically heated wire, but nitroglycerine, picric acid and dynamite require to be confined in a small space and struck a sharp blow before they explode. In general the best way to set off an explosive is to make use of the tremendous pressures—400,000 pounds to the square inch—produced by the detonation of fulminate of mercury, and this is the method which is almost invariably adopted

in practice. The detonator is ignited either by striking, as in a rifle or gun, or by means of a fuse or heated electric wire ; the very rapid decomposition produces an explosive wave which stimulates the disintegration of the main explosive. It is interesting to note that the pressure of an explosive wave which is produced at one point may cause the explosion of adjacent materials ; thus if a series of dynamite cartridges are arranged in a row at a distance of about 1 foot apart, and the first only is exploded by means of a mercury fulminate cap, then all the others will explode spontaneously in rapid succession. In order to avoid this danger of induced explosions mounds are generally built between different buildings in an explosives factory so that the explosive wave may be deflected and its force broken.

Before leaving the subject of explosive materials, it would be well to say a little concerning their manufacture. Gunpowder generally consists of 75 per cent. of potassium nitrate, although sometimes sodium nitrate is used, 10 per cent. of sulphur and 15 per cent. of carbon ; the process of manufacture chiefly consists in mixing the ingredients very thoroughly, and of forming the resulting mass into grains of different sizes, as required for different purposes. Nitroglycerine<sup>1</sup> was first made in 1847 by an Italian, Sobrero, by the action of a mixture of strong nitric and sulphuric acids on glycerine ; it is a heavy, faintly yellow liquid. It was originally used only as a medicine in small amounts because it was regarded as too dangerous to handle as an explosive, but in 1863, a Swede, Alfred Nobel, succeeded in applying it industrially. Several serious explosions occurred, however, and the manufacture of nitroglycerine was prohibited almost universally until Nobel discovered that by mixing this explosive liquid with an inert infusorial earth, known as ' kieselguhr ', a solid high explosive could be obtained which could be handled with all reasonable safety. The resulting substance was called ' dynamite ', and it is probably one of the most important explosives of the day ; modern dynamite, however, no longer contains the inert kieselguhr as the absorbing medium, but wood-pulp is used instead together with some nitrate. This form of dynamite is just as safe as the original form but it carries no inert matter to reduce its explosive effect since the wood-pulp can be completely burnt up in the explosion.

<sup>1</sup> More accurately called ' glyceryl nitrate '.

The next explosive to consider is gun-cotton or nitro-cellulose,<sup>1</sup> made by treating purified cotton with mixed nitric and sulphuric acids ; if the acids are thoroughly well washed out of the finished material it can be handled with safety, especially if wet. Various forms of nitro-cellulose are also used in the manufacture of celluloid, cinema films, and the so-called ' cellulose ' lacquers which are being extensively used at the present time.

One of the most important high-explosives for military purposes is picric acid which forms the basis of ' lyddite ' and ' melinite ' ; by acting on phenol (carbolic acid) first with strong sulphuric acid and then with nitric acid tri-nitro-phenol, which is the chemical name for picric acid, is produced. This substance was originally used almost entirely as a yellow dyestuff, and even now it is used for the treatment of burns in medicine ; ' picric gauze ' is particularly well known. As an explosive picric acid is being replaced to a great extent by T.N.T. (tri-nitro-toluene), made by heating toluene, obtained from coal tar, with nitric and sulphuric acids under suitable conditions. T.N.T. has several advantages over picric acid ; it has a lower melting point and consequently is more easily filled into shells ; it is much safer to make and handle, and it does not combine with metals to form dangerously explosive salts as does picric acid. Various mixtures of T.N.T. and ammonium nitrate were used to a large extent during the Great War.

Almost nothing has been said so far concerning gaseous explosions, except with regard to their avoidance in coal mines, but the explosion of a mixture of gases is the fundamental phenomenon in the internal combustion engine, which is having such an important influence on our social life, and has made aviation possible. It is well known that although coal gas can be made to burn quietly at a jet, if a light is applied to a mixture of coal gas and air an explosion will occur ; in the same way petrol vapour may be allowed to burn at a jet, but if an electric spark is passed through the mixture with air the chemical action, or combustion, takes place almost at the same instant throughout the whole mixture and an explosion results.

In the motor-car engine a mixture of air and petrol vapour is drawn from the carburettor into the cylinder where it is compressed, and then an electric spark is passed through the

<sup>1</sup> More accurately called ' cellulose nitrate '.

mixture by means of a sparking plug. The heat of the spark causes the vapour to ignite, and there is a sudden explosive liberation of large amounts of very hot gases which push back the piston. The work done in this way is utilized by a suitable mechanism to propel the car. If the mixture of air and petrol vapour is compressed too much before it is exploded by the electric spark then an extremely rapid reaction which we have already termed a 'detonation' occurs (p. 111). This produces the effect of 'knocking' or 'pinking', as it is often called, and the motorist knows that it is then time to 'retard the spark', so that the explosion takes place before the air-petrol mixture is too greatly compressed. In order to obtain the maximum efficiency from the fuel used in a motor engine it is desirable, theoretically, to compress the mixture as much as possible, but in practice the danger of knocking sets a limit to this.

It was found in 1922, by the American chemists Midgley and Boyd, that the addition of small amounts of certain substances, like tetra-ethyl lead, to the petrol would prevent knocking and so allow a higher compression with increased efficiency. 'Ethyl petrol', which was only introduced into Great Britain quite recently, has been in use in the United States for some time; in fact in the latter country 500,000,000 gallons were sold during 1927. This petrol contains about 1 part in 1,300 of tetra-ethyl lead, together with some ethylene dibromide, which prevents the lead from attacking the porcelain of the sparking plugs; the mixture has definitely anti-knock properties but it is an open question as to whether the fuel is economically worth while at the present time, since the compression possible in the majority of motor-car engines does not allow the full benefit of the fuel to be realized. The poisonous nature of the tetra-ethyl lead itself has retarded to some extent the general adoption of the new fuel in this country, but the problem of getting the best efficiency from the limited supplies of motor fuel available is likely to be taken more seriously in the near future. It is interesting to mention that benzol, alcohol and methyl alcohol—the liquid fuels of the future (p. 197)—do not produce knocking, and when a new engine with a high compression is designed, these fuels, as well as petrol specially treated with an anti-knock reagent, will play an important part in both road and aerial transport.

## QUESTIONS

1. What are the probable causes of the luminosity of a candle?
2. Explain the difference between a luminous and a non-luminous gas flame.
3. What is an explosion?
4. Name some common explosives and indicate how they are made.

## SUBJECTS FOR ESSAYS AND DISCUSSION

1. The invention of the Davy lamp for use in mines.
2. The nature and uses of high and low explosives.
3. The development of safety explosives for use in coal mining.
4. The cause and prevention of 'knocking' in the internal combustion engine.

## FURTHER STUDY

1. The study of explosive reactions in peace time.
2. The work of Davy which led up to the discovery of the safety lamp and more recent developments.
3. The avoidance of gas and dust explosions in industry and in the home.
4. The importance of 'compression' in the internal combustion engine.

## BOOKS TO READ

- Old Trades and New Knowledge. Bragg. (Bell.)  
The Chemical History of a Candle. Faraday. (Dent.)  
Chemistry in Industry. Vol. II. (Chemical Foundation, New York.)  
Chemistry Applied to Home and Community. Beery. (Lippincott.)  
Chemical Discovery and Invention in the Twentieth Century. Tilden. (Routledge.)  
Outlines of Industrial Chemistry. Thorp and Lewis. (Macmillan.)  
Industrial Chemistry. Vol. II. Rogers. (Constable.)

## SUGGESTIONS FOR EXPERIMENTS

- Examination of different types of flames.  
Effect of varying the amount of air in an air-gas burner.  
Explosion of mixture of hydrogen and oxygen.  
Burning hydrogen without explosion.  
The working of an internal combustion engine.

## CHAPTER X

### OUR DAILY FOOD: ENERGY REQUIREMENTS

ONE of the most remarkable powers of a human being, or an animal, is the ability to absorb certain food materials and to transform them into the particular substances required for its own growth and development. In attempting to analyse scientifically the processes of digestion and assimilation of food, we appear to be faced with a hopeless task because of the great differences between different human beings. Two people may eat exactly the same food: one will become fat whilst the other remains thin; one may suffer from indigestion whilst the other digests his food with the greatest of ease. The whole problem, therefore, is one of very great complexity, but in spite of this a number of phenomena which are common to all living beings, have been observed and studied. In this chapter some account will be given of the fundamental principles involved in the utilization of food material by the human and animal organisms.

In the course of daily life a human being is continually using up energy; any muscular activity, no matter how slight, requires the expenditure of a certain amount. Even during sleep, energy is still necessary for the performance of the essential processes of breathing and of circulating the blood through the veins and arteries; the utilization of energy, or in other words the performance of work by the body, therefore, never ceases during life. Further, since the temperature of the body is always greater than that of the surrounding air, we are continually radiating heat away from ourselves and an exactly equal amount must be continuously supplied in order to maintain the normal body temperature of  $98.6^{\circ}\text{F}$ .

Now it is a fact of scientific experience that energy can be neither created nor destroyed, and hence as far as we are aware no work can be done or any form of energy, such as heat,



produced unless an exactly equivalent amount of some other form disappears. That is, one form of energy can be transformed only into an equivalent amount of another form, and an engine is an instrument for performing this transformation. Thus in the steam engine the energy stored away in coal—energy which came to the earth from the sun millions of years ago—is converted into mechanical work. In the petrol motor, also, we have a familiar instrument for transforming energy ; a chemical reaction takes place between petrol vapour and oxygen from the air resulting in the production of a large volume of hot gases which push back the piston. The energy of the chemical action is by this means converted into mechanical work and can be utilized, by suitable mechanism, for propelling a motor car. This energy must have been latent in the petrol and it was probably stored up in the following way. Millions of years ago certain living things—animal and vegetable—which had built up into themselves either directly or indirectly the energy of the sun, died and decomposed. In the course of time the decomposing matter became converted into petroleum oil, from which petrol is obtained (p. 183) and this still contains some of the original energy of the living creatures in a latent condition. The energy of plant and animal material, or more correctly the energy of the sun, of millions of years ago is thus stored up in a sort of treasure chest, which we call petrol, and the internal combustion engine is the key which opens the chest and makes this energy of æons ago available for use to-day.

The human engine, as far as we are aware, is like all other known engines : it can only transform energy ; like the steam engine and the petrol motor it requires fuel which contains latent energy locked up in it. This fuel is clearly the food we eat, and as a result of chemical actions which take place in the body the energy is set free and may be utilized for doing work and keeping the body warm. Almost all the energy present in food must have come originally from the sun, because nearly all our food is ultimately of plant origin, and we have already seen (p. 101) that green plants can store up the energy of sunlight in the form of complex chemical substances ; even the fleshy foods we eat are derived from animals fed on vegetable matter. If the human engine cannot create energy, we must try to discover next exactly how much energy is required for the adequate performance of a day's

work and then the quantity of food required to supply exactly that amount of energy.

The first part of the problem has been attacked in two distinct ways. In one method the human being is placed in a special closed chamber called a 'calorimeter'—that is, a heat measurer. The subject is supplied with normal food and air, and the heat which he produces in the course of various methods of living can be carefully measured; this heat is exactly equivalent to the amount of energy which is used up. In this way the expenditure of energy during resting, sleeping, writing or working may be determined. Unfortunately the apparatus is complicated, and the subject of the experiment is confined under rather restricted conditions in which only a limited number of actions can be performed. In the second method these difficulties are overcome; the amount of oxygen used in a given time is measured, and since it is known that a given volume of oxygen corresponds to a certain amount of energy expended, then the total amount of energy required under various circumstances can be determined. The method of measurement is to fit the subject with a nose-clip so as to compel him to breathe through the mouth; the mouthpiece is fitted with a valve which allows fresh air to be breathed in from outside, but sends the expired air into a bag whence it can be removed, the volume measured and analysed. From the volume and analysis the original volume of air breathed in can be found and the amount of oxygen used in breathing can be calculated. This method has great advantages, since the measurements can be made whilst running, swimming, cycling or performing many kinds of mechanical work which are impossible in the calorimeter.

As a consequence of these two methods of experiment, some very interesting and important results have been obtained, but before we can give an account of them it is necessary to decide on some unit in which to express energy; just as we express weight in pounds or grams, length in inches or centimetres, we express energy in terms of Calories. The Calorie is really a heat unit, but since heat is a form of energy, and as a matter of fact bodily energy is almost invariably measured in the form of heat, it will do very well for our particular purpose. The amount of energy, as heat, required to raise the temperature of 1 kilogram ( $2\frac{1}{2}$  pounds) of water 1 degree Centigrade, or as mechanical work, necessary to lift

3,070 pounds through a height of 1 foot, is equal to one Calorie. The following table gives the rough average hourly expenditure of energy by an average-sized man, 154 pounds in weight, under different conditions :

	Calories per hour.		Calories per hour.
Sleeping . . . . .	60-70	Carpentry, metal work,	
Awake, lying still . . . . .	70-85	painting . . . . .	240
Sitting at rest . . . . .	100	Walking $3\frac{1}{4}$ m.p.h. . . . .	300
Standing at rest . . . . .	110	Sawing wood . . . . .	480
Typewriting . . . . .	140	Running $5\frac{1}{4}$ m.p.h. . . . .	500
Walking $2\frac{1}{2}$ m.p.h. . . . .	200		

The energy expenditure of a man completely at rest and lying down, at least twelve hours after a meal, is called the 'basal metabolic' rate and is equal to 68 Calories per hour when awake and 62 Calories when asleep.

If we consider an average man who works eight hours a day at a not too heavy job, on which he expends 200 Calories per hour, has eight hours' leisure in which he probably uses up 105 Calories per hour, and sleeps for eight hours using 65 Calories per hour, his total energy expenditure for a whole day is 2,960 Calories. As a matter of fact 3,000 Calories is frequently considered as the daily energy expenditure and requirement of an average man; those who do strenuous manual work clearly expend more energy, whilst a sedentary worker, such as a clerk, uses up somewhat less. A woman apparently only requires 83 per cent. of the energy expended by a man for the same amount of work, as the basal metabolic rate is lower. In cold climates more heat has to be supplied to the body to make up for the severe losses by radiation, and hence the energy requirement may go up to 7,000 Calories per day, whilst in hot countries it is generally down to 2,500. For the purposes of subsequent discussion, however, we will take the value of 3,000 Calories as the average daily expenditure of energy by any average human being.

We have now to discover the energy content of various foods in order to determine the amount required to replace the energy expended during each day. The determination is carried out in an apparatus called a bomb calorimeter; this is a strong steel vessel in which a weighed amount of pure food material may be completely burnt up by means of oxygen, and the heat produced determined accurately. The heat liberated in this way is a measure of the total amount

of energy which would be available if the food were completely used up by the human being ; in actual practice, however, there is always a certain amount of wastage due to the incompleteness of combustion in the body, and allowance has to be made for this in calculating the energy content of food materials. As a result of these measurements, it has been found that 3,000 Calories, the amount of energy used up by a man per day, is contained in  $\frac{3}{4}$ -pound of lard or olive oil, in 1 pound 10 ounces of sugar or in just less than 3 pounds of beef steak. Now it does not need a chemist or a physiologist to tell us that if we tried to feed a human being, or an animal, entirely on sugar, or on lard, he could not live for very long, and the reason is that the human being must have a variety of food materials for the normal life processes to continue. Calories are important certainly, but they are not the only factor ; investigation has shown that all the common food-stuffs contain one or more of three types of chemical compounds. These are called carbohydrates, fats and proteins, and life can continue satisfactorily only if there is a definite amount of each of these three groups of substances in the food material.

The carbohydrates of food are generally starches and sugars ; these are found in cereals and cereal products, e.g., flour and bread, potatoes and other root vegetables, sugar, honey and sweet fruits. On combustion in oxygen, 1 pound of carbohydrate, which contains only the elements carbon, hydrogen and oxygen, will yield on the average 1,860 Calories of energy and the waste products are merely carbon dioxide and water.

Fats may be either of vegetable or animal origin ; they may be hard fats, such as suet, mutton fat and lard, or they may be liquid fats—often called oils—such as olive oil, cotton-seed oil, etc. The chief sources of fats are milk, butter, vegetable oils, and portions of fish and meat. These substances, like carbohydrates, contain the elements carbon, hydrogen and oxygen ; they yield 4,218 Calories of energy per pound on complete combustion, but although the energy yield per pound is greater they are not so readily oxidized in the body as are the carbohydrates. These latter, therefore, act as the chief fuel material, whilst the fats are in a sense subsidiary.

The proteins are very complex chemical substances ; they always contain carbon, hydrogen, oxygen and nitrogen, and

generally sulphur or phosphorus in addition. They are found chiefly in meat, fish, milk, eggs, peas, beans, nuts, and to a small extent in cereals and vegetables. On complete combustion 1 pound of protein will, on the average, yield 1,860 Calories, but the chief function of protein in the body is not to act as a fuel; it is the only type of food material which contains nitrogen, and this is required for the renewal of tissues. Protein, therefore, is the substance which replaces the worn-out parts of the living creature.

In deciding the exact requirements of the body it is necessary to consider first of all the amount of protein needed to repair tissues since no other food stuff can perform this necessary function. As a result of observation and experiment, it is generally accepted in this country that an adult man requires about 100 grams ( $3\frac{1}{2}$  ounces) of pure protein per day and a woman about 95 grams ( $3\frac{1}{3}$  ounces); but these figures are not by any means universally accepted. Some physiologists consider that 120 grams per day is required, whilst Chittenden, on the other hand, as the result of a large number of experiments carried out on students and soldiers in the U.S.A., considers that normal health can be maintained on a diet containing only about 50 to 60 grams of protein per day. It is doubtful, however, if the observations were carried on for a sufficiently long period of time for the results to be conclusive; the subject may maintain apparently good health on a low protein diet for a long time, but he may be using up his reserve of tissue and eventually suffer harm. Hindhede, in Denmark, also considers that the protein in the diet may be reduced without harm, and in fact the results may be beneficial; in favour of this argument the decreased death rate in Denmark during 1917 and 1918, when protein consumption was legally restricted, is quoted. Hindhede, however, admits that the decreased production—and consumption—of alcoholic liquors during the same period may also have had some influence.

There is no doubt that the human body can accustom itself to use less protein. For example, the poorer people of Bengal, in India, are largely vegetarian and only consume about  $1\frac{1}{2}$  ounces of protein per day and seem to thrive well; further examination, however, shows that they are inferior mentally and physically to Europeans, and so the decrease in the consumption of proteins may be harmful. The problem is,

therefore, not altogether a simple one. If the human being takes in more than the 100 grams per day considered to be necessary, then the extra amount, which is not needed, can be decomposed and passed out of the system, provided the body is fairly active ; with older people, an excess of protein is often considered harmful. It is not completely digested and may be attacked by bacteria, and so produce poisons in the body.

The 100 grams of protein only supply 410 Calories, and so about 2,590 Calories are still to be provided by the carbohydrates and fats. The latter are concentrated sources of energy, but unfortunately they take long to digest ; carbohydrates are easier to digest, and for some little understood reason the utilization of fats, and to some extent proteins, in the body is dependent on the presence of a certain proportion of carbohydrate. Most diets, therefore, consist of a large proportion of these latter substances, and the daily requirement is generally taken as 400 grams (14 ounces) ; this supplies 1,640 Calories of energy. In order to supply the remaining 950 Calories, just over 100 grams ( $3\frac{1}{2}$  ounces) of fat are necessary. The average diet, therefore, should consist of  $3\frac{1}{2}$  ounces of proteins,  $3\frac{1}{2}$  ounces of fats, and 14 ounces of carbohydrates per day. When fat cannot be tolerated owing to difficulties in digestion, then the carbohydrates should be increased because an excess of these substances can be converted into fat by the body. Many of the poorer peoples of the world take advantage of this and live mainly on carbohydrates ; such is particularly the case with certain Indians, Chinese and Japanese who live mainly on a diet of rice or other grain. Some people doubt if the body really requires any fat from outside at all ; they suggest that the body can synthesize its own from other materials. There is some uncertainty on this point, but in any case it is known definitely that very little, if any, fat is required. Eskimos, on the other hand, get very little carbohydrates, especially in winter ; apparently their systems have become accustomed to produce the necessary carbohydrates from proteins, whilst the fat, as a concentrated fuel, supplies adequately the large amount of heat which these people require in a cold climate.

We now know the average daily requirement of the body in terms of carbohydrates, proteins and fats ; we must next

consider how much natural food must be consumed in order to obtain these necessary amounts. Many foods contain 60 to 80 per cent. of water, and some contain a fair proportion of mineral salts, whilst very few contain only one of the three chief constituents of the diet. It is necessary, therefore, to have a complete analysis of all food material so that we know how much of each to take in order to make up the daily energy and body-building requirements. Some of the results of the analyses and energy values of foods—the edible portions only—are given in the table on page 125. The figures show that an average mixed diet is generally likely to supply the necessary amount of fuel for the body to perform its normal functions, and to be quite adequate in carbohydrate, fat and protein content.

Having now decided upon the main requirements of the body, we must next see how these are utilized as a result of digestion. The process ultimately consists of a breaking down or simplification of the food material so that it is able to pass through the walls of the intestine into the blood stream. This disintegration is brought about mainly as a result of the action of remarkable substances known as 'enzymes' or 'ferments' (p. 157), which are produced by the various digestive juices. These enzymes are able, in suitable environment, to stimulate the chemical reactions which occur during the decomposition of food. There are a number of enzymes produced by the body, but each can help to perform one chemical process only, and since there are several different processes involved in food digestion, a number of different enzymes are required.

The first of these is encountered in the saliva which is produced from certain glands in the mouth; this enzyme is called 'ptyalin', and in alkaline solution has the power of breaking down carbohydrates into simpler substances. In the mouth, too, the food is masticated and broken up into small fragments; this not only causes it to mix up well with the salivary juices, but the small particles are more readily acted upon by the enzymes in other parts of the body, and so are easily digested. From the mouth the food passes through the œsophagus or gullet into the stomach; here there is produced the gastric juice which has an acid reaction, due to the presence of about 0.4 per cent. of hydrochloric acid, and contains the enzyme 'pepsin' which attacks only

## TABLE OF FOOD VALUES

(Adapted from Plimmer's *Analyses and Energy Values of Foods*)

Food material	Water Per cent.	Protein Per cent.	Carbo- hydrate Per cent.	Fat Per cent.	Calories Per lb.
Bacon (lean) . . . .	56	21.5	—	5.9	649
Beef (rump steak, lean)	69	21.9	—	7.3	715
„ (sirloin, lean) . . .	69	21.2	—	9.0	774
„ (liver) . . . .	71	19.9	4.4	3.2	587
Chicken breast . . . .	74	24.6	—	0.2	466
Duck leg . . . .	67	20.1	—	11.4	855
Ham (lean part) . . .	62	20.3	—	12.3	896
Mutton leg (lean) . . .	71	21.1	—	7.0	688
Pork loin (lean) . . .	66	21.4	—	11.1	866
Cod . . . .	81	17.5	—	0.1	330
Herring . . . .	68	18.6	—	10.9	806
Salmon . . . .	64	18.6	—	15.8	1,012
Shrimp . . . .	68	23.2	1.4	0.9	495
✓ Butter . . . .	14	—	—	81.6	3,442
✓ Cheese (Cheddar) . . .	34	25.2	—	33.4	1,939
Dripping . . . .	—	—	—	100	4,218
Eggs . . . .	74	12.3	—	11.3	734
✓ Marg . . . .	14	—	—	84.3	3,556
Milk . . . .	88	3.3	4.8	3.6	303
✓ Apples . . . .	84	0.3	12.5	0.2	246
✓ Bananas (Jamaica) . . .	73	0.7	17.7	0.1	434
Black Currants . . . .	81	1.3	8.0	0.2	181
Grapes . . . .	85	0.6	13.9	0.1	274
Lemons . . . .	91	0.5	3.1	0.5	88
✓ Oranges . . . .	86	0.9	9.5	0.1	198
Currants (dried) . . . .	21	1.7	42.0	0.3	826
Prunes (stoned) . . . .	28	3.0	40.4	0.3	820
Raisins . . . .	19	2.2	61.2	0.3	1,192
Almonds (Valencia) . . .	3.6	18.6	15.2	56.4	3,008
Brazil nuts . . . .	2.9	13.2	8.1	70.4	3,366
Chestnuts . . . .	44	3.0	48.2	1.9	1,032
✓ Beans (broad) . . . .	66	9.4	22.8	0.4	616
„ (French) . . . .	92	1.9	4.8	0.1	129
✓ Cabbage . . . .	93	1.4	4.5	0.1	114
Cucumber . . . .	97	0.6	2.0	0.1	52
Lettuce . . . .	95	1.1	1.9	0.2	64
Onions . . . .	87	1.3	10.8	0.1	229
✓ Potatoes (boiled) . . .	81	1.9	16.0	—	334
✓ Tomatoes . . . .	94	0.7	4.5	0.1	101
Bread (brown) . . . .	44	7.5	45.8	0.1	996
„ (white) . . . .	43	6.6	48.7	0.1	1,032
Flour (white) . . . .	11	11.1	76.1	1.3	1,686
Oatmeal . . . .	7	11.9	70.0	8.6	1,886
✓ Rice . . . .	12	6.8	80.0	0.6	1,640
Chocolate . . . .	1.0	4.8	59.9	31.1	2,515
Honey . . . .	18	0.4	71.4	—	1,290
Jam (plum) . . . .	24	0.2	70.0	—	1,306
Marmalade . . . .	28	0.2	68.6	—	1,280
Sugar (white) . . . .	—	—	—	100	1,860



proteins. In about three to four hours the stomach contents will have passed into the small intestine, and just as it enters the latter organ the partly digested food meets two distinct sets of juices coming from the pancreas (or sweetbread) and the liver respectively. The pancreatic juice is alkaline and contains three enzymes: 'amyllopsin', which simplifies the carbohydrates, 'trypsin', which splits up proteins, and 'lipase' or 'steapsin', which decomposes fats. The digestive juice coming from the liver is known as 'bile', but although this apparently contains no enzyme, it appears to act in conjunction with lipase in the decomposition of fats. The exact rôle of the bile is still a matter of uncertainty. The intestine itself also produces juices which contain an enzyme, 'erepsin', which completes the disintegration of proteins, and three carbohydrate-splitting enzymes, 'maltase', 'sucrase' and 'lactase'. In the large intestine the digestion is complete and from there the waste products, which are not disintegrated by the digestive juices, pass out of the body.

The waste materials consist mainly of cellulose, which makes up the woody and fibrous portions of fruits and vegetables and the husk of cereals, and of the indigestible fibres of meat. Although these substances are not used by the body, they play an important part in the digestion of food; they stimulate the regular movements of the intestine, probably as the result of their bulk, so that the food material moves steadily along and does not accumulate and become attacked by microbes. The undigested, and indigestible, part of food is often called 'roughage' and to this is due the laxative action of fruits and vegetables; in the absence of roughage constipation may result.

#### QUESTIONS

1. How is the energy expenditure of human beings investigated?
2. What are the three chief food materials? How may they be obtained?
3. What are the minimum average daily requirements of the main food constituents?
4. What is the average daily expenditure of energy of a man and of a woman (a) in a hot climate, and (b) in a cold climate?

## SUBJECTS FOR ESSAYS AND DISCUSSION

1. Calculate the amount of energy required each day by (a) a woman typist, (b) a carpenter, and (c) a man sawing wood, assuming that they work for eight hours, have eight hours' leisure, and sleep for eight hours.
2. An outline of the digestive process.
3. The difficulties involved in a study of the chemistry of digestion.
4. Food and energy.

## FURTHER STUDY

1. Details of the determination of the energy expenditure of human beings and of the energy content of food materials.
2. The energy content and food value of the diet of people in different walks of life.
3. Examine the types of diets of people in different parts of the world.
4. The physiology of the digestive system.

## BOOKS TO READ

- Chemistry Applied to Home and Community. Beery. (Lippincott.)  
 Science Remaking the World. Caldwell and Slosson. (Doubleday, Page.)  
 Food and Health. Callow. (Oxford Univ. Press.)  
 Chemistry of Food and Nutrition. Sherman. (Macmillan.)  
 Nutrition and Dietetics. Cathcart. (Benn.)  
 Food in Health and Disease. Harrow. (Routledge.)  
 Analyses and Energy Values of Foods. Plimmer. (H.M.S.O.)  
 Food and the Family. Mottram. (Nisbet.)

## SUGGESTIONS FOR EXPERIMENTS

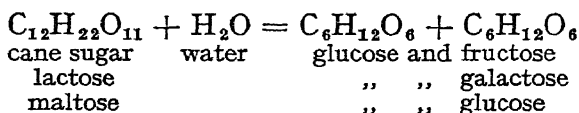
- Tests for carbohydrates, proteins and fats.  
 Examination of various food materials for the three essential constituents.

## CHAPTER XI

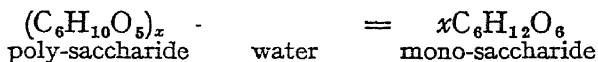
### OUR DAILY FOOD: THE CHEMISTRY OF DIGESTION

WE will consider here in more detail, from a chemical standpoint, the changes undergone by the three types of food material during digestion, and in the building up of the digested food into the living being—the process of metabolism as it is generally called; for this purpose it will be advisable to take the three classes: carbohydrates, fats and proteins, in turn.

The least complex carbohydrates are the simple sugars or, as the chemist calls them, 'mono-saccharides'; the three most important of these, from the standpoint of food absorption, are glucose, fructose and galactose. These three all have the same formula  $C_6H_{12}O_6$ , but the constituent atoms are arranged in a slightly different manner in each case. The next, somewhat more complex, group of carbohydrates are known as the 'di-saccharides'—that is, double sugars—and they may be regarded as being built up from two molecules of the simple mono-saccharides; the latter may both be the same or they may be different. The chief di-saccharides found in foods are sucrose, or cane sugar, which is a combination of glucose and fructose; lactose, or milk sugar, built up from galactose and glucose; and maltose, or malt sugar, which is based on two molecules of glucose. Each of these di-saccharides has the formula  $C_{12}H_{22}O_{11}$ , which is equivalent to two molecules of mono-saccharide ( $2 \times C_6H_{12}O_6$ ) minus one molecule of water ( $H_2O$ ); that is  $C_{12}H_{24}O_{12} - H_2O$  equals  $C_{12}H_{22}O_{11}$ . On boiling with a dilute solution of an acid, like hydrochloric acid, or by the action of the appropriate enzyme, the double sugars undergo a change called 'hydrolysis'; this means that each molecule of sugar takes up a molecule of water and breaks up into its two constituents. Thus:

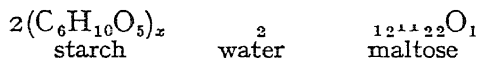


When a large number of simple sugar molecules are built up into a complex molecule, we obtain a 'poly-saccharide'; these have the general formula  $(\text{C}_6\text{H}_{10}\text{O}_5)_x$  where  $x$  is an indefinite whole number. If  $x$  is large—we do not really know how large—then the substance may be a 'starch' or a 'cellulose'; cellulose is one of the main constituents of wood and cotton, and it is also found in the woody and fibrous parts of plants and vegetables. In the starches the atoms appear to be arranged differently from those in the celluloses, and so the properties are different. If  $x$  is somewhat smaller than in the starches, we get the 'dextrins'. All these polysaccharides may be hydrolyzed by long boiling with acids, or by means of suitable enzymes, and eventually simple sugars, mainly glucose, are formed; thus



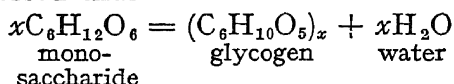
Cellulose, being one of the most complex, is naturally very difficult to hydrolyze; human beings do not produce the requisite enzyme, and so it passes out of our systems unchanged, but certain living organisms, such as the snail, are apparently able to decompose it to some extent. The digestive glands of the human body, however, produce the enzymes necessary for the complete hydrolysis of starch to glucose.

In the process of digestion of carbohydrates, the first step is brought about by the ptyalin of the saliva, which acts best in a weakly alkaline medium and not at all in the presence of acid; this has the power of partly hydrolyzing starch to form maltose, thus:

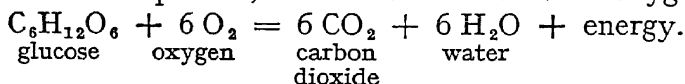


This process occurs in the stomach but here the gastric juice, which is acid, slowly penetrates into the masticated food and, by neutralizing the alkali of the saliva, gradually stops the reaction before the starch is completely decomposed. It has been estimated that the ptyalin continues to act in the stomach for about half an hour so that a fair proportion of the starch is digested there, but the rest remains unchanged

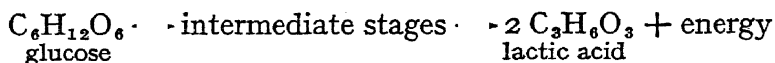
until the food enters the intestine. The enzymes amylopsin of the pancreatic juice, and maltase, sucrase and lactase of the intestinal juices, then complete the decomposition or hydrolysis of the carbohydrates—starches, dextrans and disaccharides—into simple mono-saccharides, the most abundant of which is glucose (equation, p. 129). The digestion of the carbohydrates is now complete and the simple sugars formed are all soluble in water; the solution so formed passes through the walls of the intestine into the blood, and the latter then enters the liver. The sugars are stored up in this organ in the form of 'glycogen', an animal starch having like vegetable starches the general formula  $(C_6H_{10}O_5)_x$ ; the process is thus the exact reverse of hydrolysis and is apparently also brought about by an enzyme. The reaction may be expressed thus:



The liver contains the reserve of glycogen eventually used as fuel by the muscles; it is supplied, when required, by the following mechanism. The glycogen of the liver is hydrolyzed to glucose which passes into the blood stream and is then carried round the body to the particular muscle which has used up its supply; here the glucose is built up once more into a glycogen similar to and possibly identical with that of the liver. The glycogen remains in the muscle until the latter is called upon to do some work; it is then probably split up once more into glucose and the latter combines chemically with the oxygen carried round the body by the red blood corpuscles (p. 100). The heat and energy released in this process are utilized by the body in order to maintain its warmth, and by the muscle in doing work. The equation of the oxidation process, that is the reaction with oxygen, is:



The carbon dioxide waste product passes back into the blood and is exhaled from the lungs. This process is not quite as simple as the equation indicates, as there are a number of intermediate stages; one of these is the formation of lactic acid, the acid which is present in sour milk. We thus have;



The lactic acid is subsequently oxidized to carbon dioxide and water to some extent, whilst the remainder is re-converted into glycogen. During a period of intense muscular activity, or exertion, the blood does not bring up oxygen fast enough to 'burn up' the lactic acid and so the latter accumulates; this causes fatigue, and the muscle gets stiff and tired and unable to work until enough oxygen is brought up to oxidize the lactic acid. When the latter is removed, the muscle can function once more, provided that it still contains some glycogen.

In a normal human being the glucose only passes out of the liver into the blood when it is required to replace a shortage of glycogen in any muscle, otherwise the sugar remains in store ; the result is that the amount of glucose in the blood remains remarkably constant at 0.1 per cent. Some people, unfortunately, do not appear to have the power to store in the liver the sugar which they do not require for immediate use, and hence this all enters the main blood stream and produces the disease known as 'diabetes'. Until recently the only treatment available in such cases was to reduce the carbohydrate in the diet ; this, however, had a harmful effect on the metabolism of fat (p. 134), and so the situation was complicated further.

A few years ago it was found that the amount of sugar in the blood was regulated by a secretion, produced and stored in certain parts of the pancreas, called the 'Islets of Langerhans', which was discharged straight into the blood stream. This secretion, on account of its origin, is called 'insulin' and its function is very remarkable; it apparently regulates the sugar content of the blood and prevents its variation from the normal value of 0.1 per cent. If, as a result of consuming carbohydrates, there is an excess of sugar in the blood, then enough insulin is released to induce storage in the liver and in various muscles as glycogen; a shortage of sugar in the blood is apparently readily replaced from the liver. Insulin is an example of a group of substances produced by the ductless, or endocrine glands, which are called 'hormones'; they are chemical messengers or regulators of the body. Adrenaline and thyroxine are other hormones which will be discussed later (Chap. XIX).

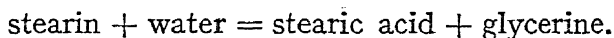
In diabetic people the carbohydrate mechanism is upset

because the pancreas is diseased and there is no production of insulin. Consequently the idea was conceived that insulin might be extracted from the normal pancreas of a dead animal—sheep, ox or pig—and injected into the blood of the patient. Unfortunately the task of extraction proved a difficult one, because the hormone is very readily destroyed by the actual enzymes produced by the pancreas, but in 1921 Banting and Best, working at the University of Toronto, devised a method for producing a stable pancreatic extract free from toxic properties and suitable for administration to human beings. The injection of this extract of insulin into the blood stream in appropriate amounts allows the normal carbohydrate metabolism to occur and all the diabetic symptoms disappear; glycogen is deposited in the liver and in the muscles, and becomes available for supplying energy to the body. The insulin treatment, however, seems to produce no improvement in the pancreas, so that the injections must be continued throughout life, but the miraculous improvements which have been observed in the health of sufferers from diabetes greatly compensate for the trouble involved. Insulin must only be used in carefully regulated amounts, as an excess of this hormone in the blood stream will cause the sugar content to fall below 0.1 per cent., with the consequent onset of faintness due to hypoglycæmia.

Since 1921 the method of extracting insulin from the animal pancreas has been greatly improved, and hence the price of this invaluable material has been reduced considerably, and a purer product is available. Attempts have been made to obtain the active constituent of the gland secretion in an absolutely pure condition so that its formula and constitution may be determined and possibly its synthesis attempted. One or two claims have been made to the production of insulin crystals, but there is still some doubt as to whether these substances really are the pure hormone. The evidence so far indicates that it is a protein derivative containing sulphur and the formula suggested indicates that it is a fairly complex substance which would not be easy to synthesize. In spite of the obvious difficulties, it is still the dream of the chemist to prepare pure insulin in the laboratory and so be independent of the material obtained from the pancreas of animals. Although success in this direction may

be far off, some interesting results are being obtained in other directions. A chemical substance called 'synthalin' has recently been prepared in the laboratory; it is a derivative of an organic base known as 'guanidine', and although it probably has no connexion with insulin, it is able to reduce somewhat the amount of sugar in the blood. Unfortunately, it does not allow the glucose to be stored in the liver as glycogen and in any case it only acts in doses which are poisonous. Although synthalin was at one time hailed as a possible insulin substitute it is now realized that it cannot be regarded in this light, but that its effects are due to a toxic action on the liver. The discovery of a substance with the same effect on carbohydrate metabolism as insulin would mark a great advance in medical chemistry.

All fats are compounds of glycerine and an acid belonging to the group known as fatty acids. The chief acids which are concerned in the common fatty foods are palmitic acid ( $C_{16}H_{32}O_2$ ), stearic acid ( $C_{18}H_{36}O_2$ ) and oleic acid ( $C_{18}H_{34}O_2$ ); the glycerine compounds, or 'glyceryl esters' as the chemist calls them, are generally known as palmitin, stearin and olein respectively. Hard fats contain the first two of these three compounds, whilst olein is a liquid fat and is the chief constituent of olive oil. Fats can be hydrolyzed by means of super-heated steam, or by boiling with acids, or else by certain enzymes; they are split up into their constituent fatty acid and glycerine; thus:



If some alkali is present during hydrolysis, as is the case in the intestine, the stearic acid, or other fatty acid, will be neutralized and a salt known as a stearate (or palmitate, or oleate) will result; these salts are commonly known as soaps (p. 85), and they assist, to some extent, in the metabolism of fats.

In the process of assimilation of food the fatty materials are almost unchanged until they reach the small intestine where they meet the enzyme lipase in an alkaline medium; in the presence of this enzyme the fats are hydrolyzed to form fatty acids and glycerine. The bile from the liver apparently plays some part in this hydrolysis, but its exact function is unknown; it may make the lipase more active or it may possibly act by helping in the disintegration of the fat particles



so that they are more easily acted upon by the intestinal juices. Some of the fatty acid is neutralized by the alkali present to form a sodium salt, or soap, and this has the power of breaking up the fatty particles into tiny globules which are more rapidly hydrolyzed.

When digestion is complete the fats have been entirely changed into fatty acids, soaps and glycerine ; these substances are absorbed into the intestinal walls and here they are built up again into the glycerine compounds of the fatty acids characteristic of human fat.<sup>1</sup> The resulting fat globules then pass through various channels until they find their way into the blood stream through a large vein at the base of the neck ; fats, as we shall soon see, are thus the only digested products that do not pass through the liver. The blood then carries the globules of fat round the body ; some of the material apparently undergoes decomposition immediately and supplies a certain amount of heat and energy, but the remainder is stored in various tissues and acts as a fuel reserve. In the event of a shortage of food, the organism draws on the fat which has been stored up in the adipose or fatty tissue ; this occurs noticeably in periods of fasting—for example, during the hibernation of certain animals. The exact method by which the energy of fat is made available for the body is still obscure ; all that is definitely known is that the fat can be burnt up, or oxidized, by the oxygen in the blood, to form merely carbon dioxide and water, with the consequent liberation of heat and energy.

It is also known that carbohydrates play some part in fat metabolism ; if the former are not properly metabolized, or if they are absent from the diet, the process of oxidation of the fat is not complete, and poisonous substances, known as 'acetone bodies', accumulate and cause biliousness. It is, therefore, necessary to have a balance between carbohydrates and fat in our food ; the habit of eating bread or potatoes with fatty meat may be instinctive, or it may be the result of more recent experience, but in any case it is a very good one. People suffering from diabetes are unable to assimilate carbohydrates and hence if they are fed on fat and protein only, they produce the harmful acetone bodies and 'acidosis'

<sup>1</sup> The exact process of building up this fat is obscure because these fatty acids may be quite different from those present in the original fatty food.

results. The injection of insulin into the system allows carbohydrates to be metabolized in the normal way, and then the oxidation of fats can be completed right down to carbon dioxide and water. It is worth noting that fats do not commence to be appreciably digested until the food enters the intestine—this may be three to four hours after a meal—hence fatty foods are regarded as the most ‘indigestible’.<sup>1</sup> Fried food is impregnated with fat, and so also is all the so-called greasy ‘rich’ food, and hence these take a long time to digest; for the same reason fat pork takes longer to digest than other meat.

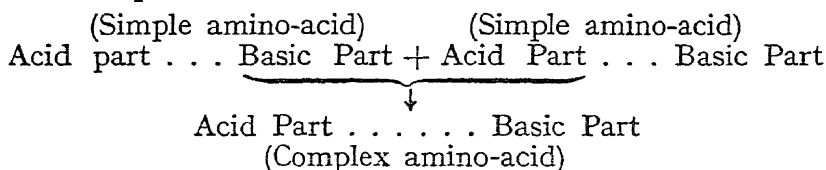
Proteins are rather like polysaccharides in the sense that they are all built up from a few simple units; the units in the case of proteins are known as amino-acids. These substances are rather curious since each molecule contains not only

the grouping of carbon, hydrogen and oxygen  $\left( -\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \end{array} \right)$ ,

which is characteristic of an acid (p. 24), but at the same

time it contains the grouping  $\left( -\text{N} \begin{array}{l} \nearrow \text{H} \\ \searrow \text{H} \end{array} \right)$  which confers basic

properties. The basic part of one molecule of amino-acid is capable of neutralizing the acid part of the molecule of another perhaps different amino-acid and in this way a more complex amino-acid is formed, thus:



The resulting complex amino-acid may become even more complex in the same way, and so a number of substances of increasing complexity can be obtained. This building up, although it cannot be carried very far in the laboratory, actually occurs in nature, and proteins are formed in this manner; the proteins always contain carbon, hydrogen, oxygen and nitrogen, but usually they also include in the very complicated molecules, containing hundreds of atoms, a

<sup>1</sup> Strictly speaking, ‘indigestible’ food is material which the body *cannot* digest *at all*; fats merely take a long time to digest.

few atoms of sulphur or occasionally phosphorus. As a result of hydrolysis which can be brought about by certain enzymes, e.g., pepsin and trypsin, the proteins can be split up step by step until the simplest amino-acids are obtained; three intermediate stages are known as proteoses, peptones and polypeptides. The hydrolysis can also be carried out by means of dilute acid, and in this way it is possible to decompose proteins in the laboratory and examine the amino-acid units from which they are built up.

So far about twenty different amino-acids have been isolated from proteins and hence the theoretically possible number of the latter is immense. Suppose we imagine a printer with a big stock of each of twenty different letters, and we ask him to string together any number up to fifty or more letters—in any order he likes—to make a series of meaningless words, using any number he chooses of each of the twenty different available letters. Every one of these complicated words would resemble a protein, and just as there would be a large number of words, so a large number of proteins are possible. The proteins required by the human body for normal growth are found on hydrolysis to yield only six or seven different amino-acids, but all of these are absolutely essential. In the absence of one or more of these amino-acids from the protein of the food, normal growth cannot continue. It has been found, for example, that when a number of rats were fed on a diet in which the only protein was the zein present in maize, the animals died; on adding the amino-acid tryptophan the rats would live but not grow, but if the amino-acid lysine was added as well, normal growth occurred.

The body is only able to prepare for itself one of the amino-acids which it requires, and that is the simplest of all amino-acids, called glycine, or amino-acetic acid; the other six or so must be supplied in the form of protein food. Proteins which contain all the necessary amino-acids—and possibly others in addition—are called 'complete' proteins, and these are found in milk, cheese, meat, fish and eggs. In our ordinary food we obtain protein from such a number of different sources, e.g. oatmeal, beans, nuts and bread in addition to the sources already mentioned, that we get a satisfactory balance of all the requisite amino-acids. Vegetarians, however, run a risk of not getting 'complete' protein unless cheese and eggs are included in the diet, and some physiologists consider that at

least one-third of the daily protein requirement of  $3\frac{1}{2}$  ounces should be of animal origin.

The digestion of protein in the body commences in the stomach; the pepsin and hydrochloric acid of the gastric juice together begin to hydrolyze the proteins to form proteoses, and these are partly converted into peptones; this decomposition is continued in the intestine by the trypsin, and later by erepsin, until the proteins are almost completely converted into the simplest amino-acids, and digestion is complete. These simple acids are soluble, and so they pass through the walls of the intestine into the blood stream which enters the liver; the amino-acids are to some extent decomposed there to form urea which is one of the waste products of the body. The rest of the amino-acids pass round the body in the blood stream and serve to renew any tissues which are worn out; it has already been mentioned that proteins are the only food materials which contain nitrogen, and so these are the real body builders and repairers. In a growing child, of course, the amino-acids are built up by the organism into the flesh, muscle, tissue, etc., required to increase the size of the body. What exactly happens to the excess of amino-acids not necessary for the renewal of wear and tear of the body is uncertain, but they are probably decomposed into fatty acids and ammonia ( $\text{NH}_3$ ). The latter and the carbon dioxide ( $\text{CO}_2$ ) in the blood unite to form urea,  $\text{CO}(\text{NH}_2)_2$ , which passes out of the body through the kidneys; the fatty acids may be built up either as glycogen, the immediate fuel of the body, or else as fats which act as fuel reserves.

Although proteins, carbohydrates and fats are the sources of energy and building material, yet the body is not made up entirely of these three types of material; it contains in addition, not only a large proportion of water, but also a number of elements required to build up the bones, and some which are contained in the blood and in the cell liquids. Water constitutes about two-thirds of the whole human body, and its chief function is as a solvent; it dissolves the digested food material, and the solution so formed can diffuse through the walls of the intestine into the blood stream. The blood is also mainly water and it holds in solution the simple sugars and amino-acids, whilst the fats are in the form of an emulsion of very tiny globules; these all pass round to the various parts of the body where they are required.

Water in a similar way carries the waste products of the body, and allows them to be eliminated in various ways.

Iron is one of the most important elements in the body since it is an essential constituent of hæmoglobin contained in the red blood corpuscles; it is also present in certain of the body proteins. Food materials containing iron in reasonable amounts are shell-fish, egg-yolk, green vegetables, fruits, beans and peas, meat, and particularly liver; an average diet, therefore, will probably contain all the necessary iron. In cases of anæmia, there is a shortage of red blood corpuscles, and it was the custom to administer iron in some inorganic form, e.g., iron carbonate. Although this iron was not absorbed into the blood it seemed to have, in some cases, a beneficial effect, possibly by preventing the wastage of the iron already in the body. In recent times an excellent cure for pernicious anæmia has been discovered in animal liver; this evidently contains a substance which allows iron to be assimilated into the blood corpuscles.

Two other important elements are calcium and phosphorus, the chief constituents of bone and teeth. Calcium salts also play an important part in the coagulation of the blood and in the working of the muscle of the heart, whilst phosphates are extremely important because they prevent the fluids in the various body tissues and the blood from becoming acid. Calcium is found in milk, fruit, nuts, and green vegetables; and phosphorus in milk, eggs, grains, beans, peas, meat, fish, fruit and green vegetables. There is thus no need to fear a shortage of either of these elements if a varied diet is consumed; in the event of a shortage, it is much better to go to the natural sources of these elements rather than to take them, as is so often done, in artificial preparations.

The body fluids also require small amounts of magnesium, potassium, sodium and chlorine; sulphur is required for building up certain proteins whilst iodine is essential for the correct functioning of the extremely important thyroid gland (p. 230). An average diet which includes fruit and vegetables will generally provide all these elements in sufficient amount.

Cooking of food serves two main purposes; in the first place the food is made much more attractive in appearance, taste and smell. This is an extremely important factor because the anticipated and actual pleasure of eating causes a free flow of the digestive juices of the stomach and the mouth

—the so-called ‘watering of the mouth’; this is, of course, an excellent preliminary to a meal as it ensures rapid digestion of the food. For the same reason, food which is disliked is generally difficult to digest. Unfortunately the requirements of the body sometimes necessitate the eating of such food, and in these circumstances it might be advisable to alternate it, at the same meal, with more attractive food; this advice applies more particularly in connexion with the feeding of children.

The second function of cooking is to break up the food material so that it is more easily attacked by the enzymes.

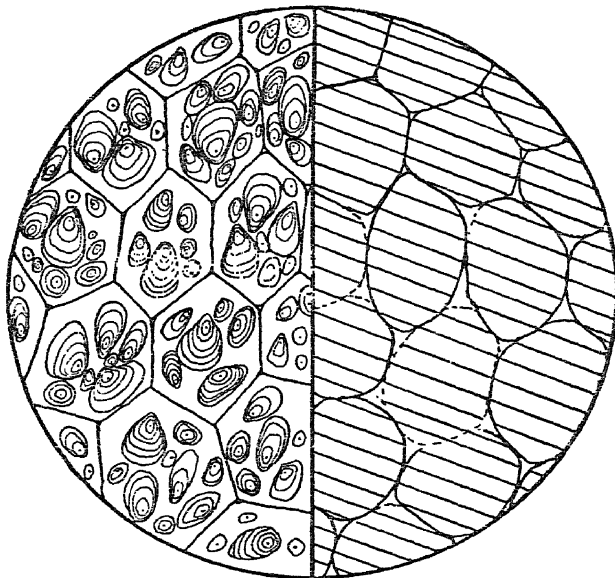


FIG. 15.—Section through a Potato (magnified)

Left portion shows starch grains before cooking; right portion shows cells filled with jelly-like material (shaded) after cooking.

Cereal and starchy foods generally contain their carbohydrates in small cells which are enclosed in a thin wall of indigestible cellulose, and hence the carbohydrate is not easily reached by the digestive juices. The effect of heat and moisture, however, in cooking is to cause the starch cells to swell and burst through their envelopes; in this way a more digestible, jelly-like product results.

In the case of meat, the principal chemical change brought about by cooking is the decomposition of the tough connective tissues, thus making the meat more tender and more readily

masticated. The net result is that the digestive juices can penetrate easily into the food, and rapid digestion can occur. As in the case of an egg,<sup>1</sup> cooking tends to harden some of the proteins of meat, and this results in a rather slower disintegration, but the advantages already mentioned probably outweigh this disadvantage.

In the cooking of vegetables the main purpose is to break up the cellulose walls of the plant cells and to make the starch more digestible; unfortunately prolonged cooking tends to dissolve out some of the valuable mineral salts, but this is often compensated for by using the vegetable water for making soups and gravies. Steaming causes a smaller loss of mineral salts, and this method of heating vegetables is becoming increasingly popular. Unfortunately, as we shall see later, cooking may have a destructive effect on the important substances called vitamins which are present in fresh food; hence it is very desirable that all those concerned with the preparation of food for the table should have some knowledge of the subject to be discussed in the next chapter.

#### QUESTIONS

1. Describe the different types of carbohydrates.
2. What is a complete protein?
3. What are the phenomena associated with diabetes?
4. How is acidosis produced?

#### SUBJECTS FOR ESSAYS AND DISCUSSION

1. The chemistry, digestion and utilization of carbohydrates.
2. The chemistry, digestion and utilization of fats.
3. The chemistry, structure and utilization of proteins.
4. The action of enzymes in digestive processes.

#### FURTHER STUDY

1. The preparation, use and action of insulin.
2. The proteins.
3. The inorganic constituents of the diet.
4. The chemistry of cooking.

#### BOOKS TO READ

Living Machinery. Hill. (Bell.)  
 Chemistry in Agriculture. (Chemical Foundation, New York.)  
 Recent Advances in Biochemistry. Pryde. (Churchill.)  
 Lectures on Certain Aspects of Biochemistry. (Univ. of London Press.)  
 Books recommended for Chapter X.

#### SUGGESTIONS FOR EXPERIMENTS

The hydrolysis of sugar, fat and protein.  
 The action of saliva on starch.  
 The 'digestion' of hard and soft egg-albumen by hydrochloric acid.

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<sup>1</sup> Egg-albumen contains proteins, and these, as is well known become hard on boiling.

## CHAPTER XII

### OUR DAILY FOOD : VITAMINS

WE have already seen that the main principles on which a diet should be based are (1) a requisite amount of fuel to supply bodily energy, (2) the correct proportion of *complete* protein for repair purposes, (3) carbohydrates and fats, and (4) certain mineral salts and water, and we naturally ask whether the fulfilment of these requirements only would be sufficient to allow normal growth and development to occur. As long ago as 1881, Lunin, a German physiologist, declared that 'substances other than casein (protein), fat, milk, sugar and salts are indispensable' to the diet, but the statement did not appear to attract much attention. Experiments were made from time to time by various people in order to find if animals could live on a purely artificial diet consisting of protein, carbohydrate and fat, and the requisite salts and water only, but the results were very conflicting. In some cases the animals, generally rats, grew normally, but in other cases they failed to do so, and it was suggested as a possible explanation that the tastelessness of the artificial food resulted in a failure of the flow of digestive juices, and so the food was not being assimilated. This explanation proved wrong because it was found by examination that the food was being digested, but curiously enough it could not be utilized by the body for growth.

The varying results obtained by different observers were due to the fact that the so-called pure diet was not always really pure, and as a result of very careful work, Professor (now Sir) Gowland Hopkins, of Cambridge University, confirmed the original observation by Lunin, and said in 1906 that 'No animal can live on a mixture of pure protein, fat and carbohydrate, and even when the necessary inorganic material is supplied, the animal still cannot flourish. The



animal body is adjusted to live on either plant tissues, or other animals, and these contain countless substances other than carbohydrate, protein and fats. It is certain that there are many factors in all diets of which the body takes account. In diseases such as rickets, and particularly in scurvy, we have had for long years knowledge of a dietetic factor, but . . . the real errors of the diet are to this day quite obscure.' In 1912 Hopkins published more detailed and convincing results of his remarkable experiments on

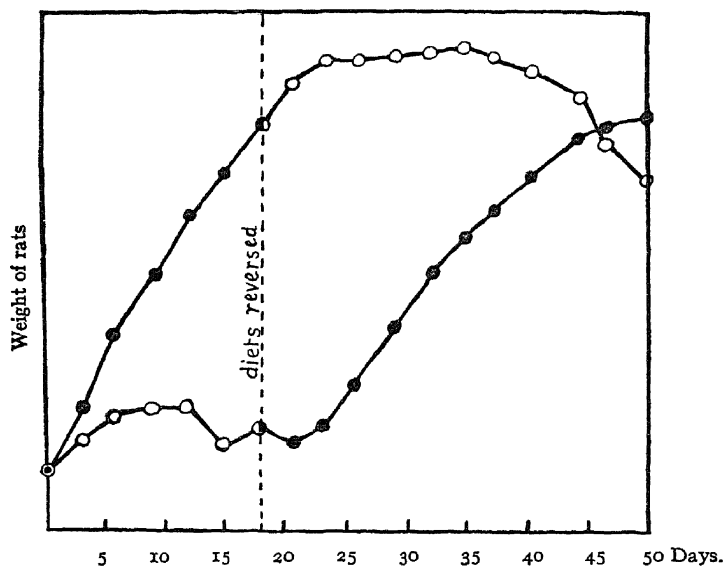


FIG. 16.—Curves showing Variation in the Weights of two Sets of Rats. Circles indicate that the rats were fed on a 'pure' diet, whilst full dots indicate that a little milk was added to this diet.

rats. He obtained two sets of eight similar rats; one set was fed on a diet consisting of purified casein (protein), sugar (carbohydrate), lard (fat) and ash from oatmeal and dog biscuits (salts), which should theoretically have been quite satisfactory, but these rats did not thrive. The other rats were fed on exactly the same diet, except that Professor Hopkins added about 2 or 3 c.c. of fresh milk to the daily ration; these grew and developed in a normal manner. Now this small quantity of milk could not have supplied

any appreciable amount of the three essential types of food stuff, nor was its energy or mineral salt content appreciable, and hence it must have contained some substance, present in a remarkably small amount, which was responsible for the stimulation of growth. In order to verify his conclusions, Hopkins reversed the diets of the two sets of rats after eighteen days; those that had been growing continued to do so for a few days more, but then they began to decline rapidly, whilst the others, which were now given milk, almost immediately began to increase in weight and continued to do so as long as this diet was maintained. Hopkins considered, therefore, that the milk contained a small amount of what he called an 'accessory factor of the diet' which added nothing to the energy content of the food stuff, but in its absence normal growth could not occur.

About the same time (1911) a Polish chemist named Funk was experimenting on the nature of the substance, present in rice germ and in yeast, which could apparently prevent polyneuritis in fowls (p. 145), and he extracted a very active material, only a very small amount of which when added to the diet, acted as a curative agent. Funk called this substance 'vitamine' because he believed, probably incorrectly, that it belonged to the group of chemical compounds known as 'amines'. It was shown subsequently that this 'vitamine' could also be regarded as an accessory food factor, and Dr. Drummond, of University College, London, then suggested that these factors should be given the general name of 'vitamins'—without the 'e', because they were probably not amines. Since Hopkins' initial discovery, much new work has been done on the subject of vitamins, and many older observations on dietetic factors have been explained in a more complete and satisfactory manner. At the present time probably six different vitamins have been identified; the absence of any one of them produces some sort of abnormality, yet only the merest traces are required in the food in order that normal conditions may be maintained. The vitamins have been carefully studied and they have been named with the letters of the alphabet, more or less in the order of their discovery; probably the most convenient method of describing them will be to discuss them in that order.

Vitamin A is found associated with animal fats, but not with those of vegetable origin, and in its absence normal

growth cannot occur;<sup>1</sup> thus rats receiving butter fat increased in weight, whilst those fed on an equivalent amount of olive oil declined and died. The vitamin is present in milk and butter, egg-yolk, mutton and beef suet, in the liver fats of herbivorous animals (ox, sheep, etc.), the green parts of plants, carrots, tomatoes and particularly in the liver oils of fish such as cod, dog-fish, halibut and salmon. Animals are apparently unable to make the vitamin themselves, but they obtain it from green plants which seem to be able to synthesize it in sunlight; the animals store the vitamin in various fatty tissues. The vitamin stored up in the livers of cod and other fish probably originates in a similar way; the cod feeds on smaller fish and these in turn feed on certain marine algæ which can make the vitamin for themselves. The vitamin content of cod-liver oil, as well as that of cow's milk, varies with the time of the year and the nature of the food of the fish or animal. In winter, for example, cows are stall-fed and their diet consists mainly of hay, oil-cake and roots; their milk then contains very little vitamin A, and it has only a very small growth-promoting activity. After the cows are put out to grass for one week, the butter made from their milk already shows, quite considerably, the power of stimulating the growth of animals.

Vitamin A is fairly readily decomposed if heated in air, owing to oxidation, but it is quite stable in the absence of air even at high temperatures. Boiling milk in an open pan, therefore, destroys the vitamin A, but the process of 'pasteurizing', which involves the holding of milk at a high temperature in a closed vessel, probably has no destructive effect. The complete absence of this vitamin from the diet not only prevents growth from taking place, but it also leads to the onset of an eye disease in children, known as xerophthalmia; this disease was particularly prevalent in Roumania towards the end of the war when there was a great shortage of fresh milk. Adults are liable to suffer from night-blindness if their food is deficient in vitamin A; in an average diet containing milk, butter, eggs, vegetables and salads, however, a shortage is extremely improbable. With growing children the problem is more serious, as they need the vitamin more urgently, and in winter

<sup>1</sup> Green and Mellanby consider that vitamin A protects against infections and so promotes growth *indirectly*. (Oct. 1928.)

when the milk and butter are deficient in vitamin A, it may be advisable to administer cod-liver oil. An excess of vitamin in the food does not cause abnormal growth; all above a certain small minimum requirement is simply not used. Human beings and animals have the power of storing vitamin A to some extent in their bodies to act as a reserve during a shortage, and so the effects of a diet without it would not be felt for some time.

It had been known for many years that the disease of the nerves called beri-beri, which is particularly prevalent in East Asia amongst peoples who live mainly on a diet of fish and polished rice—that is, rice from which the husk and germ have been removed to improve the appearance—was connected in some way with their food. Originally the disease, which led to paralysis and frequently death, was believed to be due to an infection until Takaki, a Japanese naval doctor, showed in 1882 that it could be cured by making certain dietary changes. At that time beri-beri was a common disease amongst Japanese sailors, whilst European sailors were quite immune, and Dr. Takaki thought this was because of the lack of protein in the Oriental diet. In order to test his theory, a training ship with 276 men on board was sent out on a regular cruise of nine months, and the men were fed on the usual diet rich in rice; 169 cases of beri-beri developed, and of these 25 succumbed. A short time later a similar ship was sent out on the same route, but the sailors' diet was changed so as to include more milk and meat but less rice; in this second ship only 14 men developed beri-beri, and these had all refused to adopt the new diet. This, at first sight, appeared to be a triumphant vindication of the ideas of Takaki, but he was not, as we shall see, quite correct.

The next step in the solving of the problem of beri-beri was made in Java, where the disease was rampant amongst prisoners who had been confined there. Dr. Eijkman, a Dutch physician, happened to notice one day that some fowls which had been fed on the remains of one of the hospital meals, consisting mainly of polished rice, developed a disease of the nerves called polyneuritis, the symptoms of which were very similar to those of beri-beri in human beings; when those chickens were fed with the natural unpolished rice, however, they were found to become quite normal again. Hence it appeared that the disease was definitely

connected with the diet and the curative agent was present in the husk of the rice. On investigating the cases of beri-beri in the Javanese prisons, it was found that in those institutions in which polished rice was used, one man in 39 developed the disease, but when unpolished rice was the main article of diet, the number of cases was reduced to one in 10,000. This discovery resulted in the almost complete elimination of the dread disease by the simple expedient of making the use of unpolished rice compulsory. Eijkman thought that the large amount of carbohydrate in the rice diet produced poisons which caused beri-beri, and that the husks contained an antidote for these poisons.

It was not till some fifteen years later that the real explanation was discovered; it had been found in the meantime that yeast, when added to the diet, could cure polyneuritis in fowls, and Funk attempted in 1911 to extract the active anti-neuritic principle from this substance. He worked up 200 pounds of yeast and succeeded in obtaining one-twelfth of an ounce of an extremely active substance which, administered in a dose of  $1/15,000$ th part of an ounce, could relieve polyneuritis in chickens in a few hours. Evidently the curative agent, whatever it was, needed only to be present in extremely minute amounts, and consequently it came to be regarded as one of the accessory food factors or vitamins. Funk thought that his method of extraction had given him the pure vitamin, but we know now that even his one-twelfth of an ounce was mostly impurities, so that the actual quantity of pure vitamin in a curative or preventive dose is infinitesimally small. This substance, present in yeast and in the germ of rice, and later shown to exist in the germ or embryo of other cereals, in green vegetables, tomatoes, fruit juices, peas, beans, egg-yolk, nuts and milk, was called the anti-neuritic vitamin or vitamin B by McCollum and Davis in 1915. If this is absent from the diet, then beri-beri will result in man or polyneuritis in fowls.

During the course of experiments on the feeding of rats, it was noticed that in the absence of vitamin B, although the rats might not develop beri-beri, yet they did not grow properly, nor was satisfactory health maintained; at the same time certain skin lesions were observed in the animals. It was thought, therefore, that vitamin B was not only anti-neuritic, but that it was also responsible for the main-

## VITAMINS

tenance of normal health and growth. In the last year or so, however, it has been shown that the so-called vitamin B probably contains two different factors for which the symbols  $B_1$  and  $B_2$  have been suggested. The  $B_1$  vitamin is the real anti-neuritic substance and it is easily destroyed by heating, whilst the  $B_2$  is much more stable to heat and is the growth and health-promoting factor. By heating yeast at  $120^\circ\text{C}$ . for four hours it loses its anti-neuritic property, but still retains the power of aiding growth. The vitamins  $B_1$  and  $B_2$  are not always found equally distributed; thus wheat embryo is rich in  $B_1$  and poor in  $B_2$ , whilst the reverse is the case in milk, meat, green leaves and roots. Both of these vitamins are soluble in water, and hence in the cooking of vegetables these accessory food factors dissolve in the water which is frequently poured away. If possible, this liquid should be saved and made the basis for soups and gravies; we have already seen (p. 401) that it also contains many of the valuable mineral salts originally present in the green vegetables.

It has been mentioned that the vitamin B—by this is meant  $B_1$  and  $B_2$ —is present in the germ of wheat and consequently white bread, made from the milled grain, contains very little of this principle; whilst brown bread, made from the whole wheat, does contain it. It is perhaps better not to be drawn into the controversy of white versus brown bread, but the fact remains that if vitamin B cannot be easily obtained in other ways, brown bread forms a useful source of supply. A good average diet, however, under modern conditions of life—especially if the vegetable water is utilized—contains a sufficient amount of both  $B_1$  and  $B_2$ , and so the particular bread consumed can safely be left to one's individual taste in the matter. These vitamins, like vitamin A, are built up by plants, but not by animals or human beings. Unlike A, however, they are not stored in the body to any appreciable extent, and so a shortage soon makes itself manifest.

One of the oldest of the diseases which we now know to be due to a deficiency in the diet is scurvy; it attacked the Crusaders in Palestine, and sailors have for hundreds of years suffered from its ravages. In more recent times Arctic explorers have succumbed to it, and there have also been cases in prisons and institutions in which a large number of people were fed on a poor diet. Infantile scurvy has been

quite common amongst poor children, and this was particularly so in Central Europe immediately after the last war. The symptoms of the disease are sponginess of the gums, with a resulting loosening of the teeth, brittleness of the bones, and weakness of the limbs eventually leading to paralysis. It has been known, however, for at least 200 years that fresh vegetables, or oranges, or lemons could cure scurvy, and it was only when ships had been at sea for a long time, and the sailors were compelled to live on ship's biscuit and salt pork, that the disease supervened. The knowledge that fresh foods could cure scurvy was one of the most important contributory factors in Captain Cook's successful circumnavigation of the earth in the eighteenth century; without this knowledge, his men would have succumbed and the lengthy voyages would have been impossible. In 1804 a regular lemon-juice 'ration' was made compulsory in the British Navy, and from that time scurvy amongst seamen became a comparatively rare disease. There have been occasional outbreaks of the disease from time to time, especially amongst soldiers during the war, when the diet was, to say the least of it, somewhat limited in nature.

The increasing knowledge concerning vitamins suggested that there might be an accessory factor of the diet in the absence of which scurvy developed. Experiments were made on guinea-pigs, and it was found that by feeding them on an artificial diet which included milk and yeast, as sources of vitamins A and B as well as of proteins, but did not include fresh fruit and vegetables, scurvy could be produced. The addition of a very little orange juice to the day's food soon cured the disease, and this juice evidently contains some substance, only a very small amount of which is required to prevent scurvy; this substance was called the anti-scorbutic vitamin, or vitamin C. Examination of various food stuffs showed that it was present in fresh vegetables and fruits, particularly oranges, lemons and tomatoes, and to a small extent in milk during summer. Although cereal grains and beans do not contain vitamin C, yet during sprouting—even if in the dark—the seed appears to manufacture the vitamin, and sprouted lentils were actually used as an anti-scorbutic food during the war.

Although this vitamin is present in fresh fruit and vegetables, it is rarely, if ever, present in the dried or cooked

products, for two reasons. In the first place, it is soluble in water, and so as a result of cooking it gets dissolved out and generally thrown away; in the second place, vitamin C is the most easily destroyed of all the vitamins. If it is heated in air, or even if the food material is allowed to stand for some time, the vitamin C deteriorates owing to oxidation and decomposition; in the absence of air the decomposition only occurs slowly. If food is cooked for twenty to thirty minutes, some of the vitamin C still remains, but long cooking will destroy it completely. An acid medium prevents destruction to some extent, but an alkaline liquid favours it; the addition of soda—a weak alkali—to green vegetables during cooking destroys their anti-scorbutic power. In any case it seems as if fresh fruits, green salads and tomatoes should be added to the diet if at all possible. A very active vitamin C extract has been produced from lemon-juice, and it is claimed that a daily dose of  $\frac{1}{50,000}$ th part of an ounce of this substance was sufficient to protect from scurvy a guinea-pig weighing about  $\frac{3}{4}$  pound. This extract was not a pure substance by any means, so it can be seen that of the pure vitamin only the merest trace is necessary to preserve health. Vitamin C, like A and B, can apparently only be built up by plants and not by animals or human beings. It is rather interesting to note that rats, mice and rabbits can apparently live quite well on a diet from which vitamin C is absent.

During the nineteenth century the infantile disease of rickets was unfortunately only too common in industrial towns, particularly in poor and overcrowded districts. Some medical men considered, therefore, that this disease, which results in a defective formation of bones and teeth, was due to poor hygienic surroundings, but others thought that it was due to some deficiency in the diet. Now since bones consist chiefly of calcium phosphate, it was suggested that perhaps there was not sufficient calcium in the food, and so lime water, which contains a great deal of calcium, was used in the treatment of the disease; this method was not, however, very successful. As a result of many observations it had been concluded that rickets was due to a shortage of fat in the diet, and this view seemed to be confirmed by the fact that cod-liver oil—an excellent source of fat—could cure and prevent the disease.



Dr. Mellanby, of Sheffield, described in 1918 the results of his experiments on puppies, in which he showed that rickets could be induced by feeding them even on a diet containing a large proportion of certain fats; the addition of butter or  $\frac{1}{8}$  ounce of cod-liver oil per day, however, completely cured and prevented the disease, and normal calcification of bone occurred. Rickets was, therefore, a deficiency disease, although fat was not the deciding factor, and it was considered as established that it was due to the absence from the diet of an accessory factor, or vitamin, which was present in butter and cod-liver oil. Now these are the most important sources of vitamin A, and hence it was generally accepted that the substance which prevented rickets—the anti-rachitic vitamin—was identical with vitamin A, the growth-promoting factor. By 1922, however, it began to be realized that the two factors might be different; it was found, for example, that by heating cod-liver oil in air it was no longer able to cure the eye disease xerophthalmia and promote growth, but it still possessed its original anti-rachitic action. This action is now attributed to a separate substance called vitamin D much less easily oxidized than vitamin A with which it is almost invariably associated. Certain vegetable oils, however, which contain a negligibly small amount of vitamin A have been found to have anti-rachitic properties, and so they do contain the vitamin D; butter and spinach, on the other hand, usually contain relatively more vitamin A. Cod-liver oil appears to contain about equal amounts of both, and in general the sources already given for vitamin A (p. 144) may be taken as being also those of vitamin D.

It had been observed in this country, and in the United States, that rickets in children was more prevalent during winter than in the summer, and it was suspected that possibly sunlight played some part in the normal formation of bones. As a result of experiments both on rats and on children, it was found that rickets could be cured by exposure of the body to ultra-violet light produced by means of a mercury vapour lamp or a tungsten arc; soon afterwards it was found that bright sunlight had the same curative effect. It appeared from this work that both cod-liver oil and sunlight were anti-rachitic agents; the oil could cure in the absence of sunlight, and sunlight could cure in the

absence of the oil. In the course of further observation it was found that certain food materials such as dried milk, olive and linseed oils, casein and flour, which themselves could not prevent rickets, developed anti-rachitic properties if they were exposed to ultra-violet light ; starch, sugar, glycerine and fatty acids on the other hand could not develop this property.

A careful examination showed that the materials which became anti-rachitic all contained a substance known to the chemist as cholesterol, usually associated with fats, and it was thought that the substance was the parent of vitamin D. In 1927, however, it was shown by Heilbronn, Kamm and Morton in Liverpool, by Rosenheim and Webster in London, and by others, that the source of the vitamin was another substance known as ergosterol, a minute amount of which was frequently present even in the purest forms of cholesterol. The substance ergosterol is present in the ergot fungus of rye, and it can be extracted from certain vegetable fats and from yeast, and when exposed to ultra-violet light for a short time it produces such a concentrated form of Vitamin D that 1/500 millionth part of an ounce administered daily, can cure rickets in a rat, and an even smaller daily ration is sufficient to prevent the disease ! This is the nearest approach we have made to obtaining a vitamin in a chemically pure condition.

Vitamin D is manufactured commercially at the present time by irradiating ergosterol, and the product is on the market as Radiostol pellets, one of which is said to have the anti-rachitic potency of 56 teaspoonfuls of cod-liver oil. Radiostol is also being incorporated with malt in order to give it the medicinal value of the cod-liver oil-malt mixture without its unpleasant taste and difficulty of digestion. Margarine, which is generally made from beef fat, vegetable fats and some milk, contains very little vitamins A or D, but there is obtainable to-day a margarine in which vitamin A obtained in a concentrated form from fish-liver oils, and vitamin D from irradiated ergosterol, have been incorporated ; this product is apparently just as good as summer butter and probably better than winter butter. The curative effect of sunlight on rickets is evidently due to the fact that ergosterol is present under the skin and the ultra-violet light converts it into vitamin D, and hence under appro-

priate conditions the body is able to synthesize this substance ; this is the only vitamin which the body itself can make, but unfortunately it is unable to store very much of it.

Vitamin E is the most recent accessory food factor to be detected ; in 1922 Evans, of California, and his co-workers, noticed that rats could be reared on various artificial food mixtures so that they appeared to be healthy and grow normally, but they were sterile and so unable to reproduce their species. Certain foods such as wheat embryo and the germs of other cereals, lettuce and green leaves generally when added to the diet, enabled the sterile animals to become normal and fertile. The factor responsible for fertility has been called the anti-sterility vitamin, or vitamin E. It is a very stable substance and can withstand heating without being decomposed, even in air. The vitamin is apparently present to a small extent in animal tissues, such as lean meat, in vegetable oils and to an even smaller extent in milk ; in cod-liver oil it is almost entirely absent. Our knowledge of this vitamin is not very great yet, but we do know that it can be concentrated from certain oils, and a dose of  $1/50,000$ th part of an ounce will suffice for a single litter from a female rat. An excessive dose of the vitamin E does not increase the fertility above normal ; this seems to be a general characteristic of all the vitamins. A certain small amount of each is required for normal processes to occur, but any excess over and above the minimum requirement does not have any noticeable effect on growth and development.

The study of food requirements which has led up to our modern knowledge of vitamins has, we have seen, had very important results. Diseases like scurvy and beri-beri are almost unknown to-day, whilst rickets in children should be considered as criminal. So far it appears that there are six different accessory factors necessary for normal growth and development of the living organism, and probably more will be discovered in due course. Other diseases may eventually be proved to be due to the absence of certain substances from the diet or it may possibly be shown that we have misinterpreted the observations. The fact remains, however, that results of great importance to humanity have been obtained, and no doubt will be obtained in the future, by working on the concept of the existence of vitamins.

To those responsible for the up-bringing of children a knowledge of vitamins is very important, and so it is also for those who have the arrangement of our daily food. As far as adults are concerned, there is very little danger of a shortage of vitamins, or of any other essential constituents of the diet, provided they have a good general variety of food including, amongst other things, fresh milk, cheese, fruit, salads and vegetables.

We shall see later that it is one of the ambitions of the chemist to make in his laboratory the same materials which nature makes in plants and animals; consequently he has turned his attention towards the production of vitamins. So far no vitamin has been obtained from natural sources in an absolutely pure condition and this is an essential preliminary to synthesis. The nearest approach to success has been in connexion with vitamin D, but even here the pure substance has not yet been obtained; in any case, the raw material—ergosterol—is obtained from a living organism. In due course, however, we shall probably be able to synthesize even vitamins from non-living sources.

#### QUESTIONS

1. Describe the experiments which led Hopkins to recognize the existence of the 'accessory food factors'.
2. What are the effects of a diet deficient in the various vitamins?
3. Give the chief sources of the six known vitamins.
4. How may vitamin D be obtained in a concentrated form?

#### SUBJECTS FOR ESSAYS AND DISCUSSION

1. The observations which led up to the discovery of vitamin B.
2. A vitamin complete diet with the minimum of trouble.
3. Vitamins and cooking.
4. The diet of growing children.

#### FURTHER STUDY

1. Sunlight and vitamins.
2. The experimental methods of investigating the vitamin content of food materials.
3. The possible synthesis of vitamins and the probable consequences of this achievement.
4. The possibilities of improving the vitamin content of winter butter.

## BOOKS TO READ

- Chemistry Applied to Home and Community. Beery. (Lippincott.)  
Science Remaking the World. Caldwell and Slosson. (Doubleday, Page.)  
Food and Health. Callow. (Oxford Univ. Press.)  
Nutrition and Dietetics. Cathcart. (Benn.)  
Chemistry in Agriculture. (Chemical Foundation, New York.)  
The Vitamins. Sherman and Smith. (Chemical Catalog Co., U.S.A.)  
Lectures on Certain Aspects of Biochemistry. (Univ. of London Press.)  
Medical Research Council Report: The present state of our knowledge of Accessory Food Factors. (H.M.S.O.)

## SUGGESTIONS FOR EXPERIMENTS

Owing to difficulties in technique vitamin experiments can only be carried out under the direction of experts.

Examine the charts published from time to time in various biochemical journals, in the Journal of Industrial and Engineering Chemistry (U.S.A.), and in the Journal of the Society of Chemical Industry.

## CHAPTER XIII

### CATALYSIS AND ENZYMES

IN the course of a report on the progress of physical science contributed by the chemist Berzelius to the Swedish Academy in 1835, he brought under review a number of chemical actions having one unique feature in common. All these processes appeared to be stimulated by the presence of some substance which was itself unchanged at the conclusion of the chemical reaction. For example, starch could be converted into sugar by means of dilute acid, but the acid remained unaltered in nature and amount; peroxide of hydrogen could be decomposed by the addition of an alkali, by fibrin of blood, or by finely powdered metals, all of which were quite unaffected by the decomposition process. Berzelius called this process of stimulation 'catalysis', from a Greek word meaning 'to loosen'; the substance which stimulates the reaction without itself being affected by it is called a 'catalyst', whilst the whole process is referred to as a 'catalytic' one. The word 'loosen' as applied to catalytic action is very appropriate, because we know that a catalyst acts like oil on a stiff machine. The oil loosens the bearings and makes the wheels revolve more readily, but it cannot *start* the machine; in the same way a catalyst cannot initiate a chemical process, although it makes a very slow reaction take place more quickly.

A very striking example of catalysis is based on an observation made over a hundred years ago, before the phenomenon was at all understood. If hydrogen and oxygen gases—the constituents of water—are mixed at ordinary temperatures they will unite with one another so slowly that it would probably take many thousands of years for an appreciable amount of water to be produced. On the other hand, it was noticed by Döbereiner, in 1823, that if a stream of hydrogen gas is allowed to impinge on to a piece of finely divided and

porous platinum metal—prepared by a special method—supported in the air, then the hydrogen catches fire and burns readily, producing water. The explanation of this phenomenon is that the platinum acts as a catalyst and causes the union of the hydrogen and oxygen to occur so rapidly that the heat liberated in the reaction is sufficient to raise the temperature to the point at which the hydrogen will inflame. This observation was applied in the construction of an automatic fire-lighter called Döbereiner's lamp; it consisted of a small hydrogen generator, containing zinc and acid, and a small piece of spongy platinum suspended above the jet from which the gas was emitted. When the tap was turned on a stream of hydrogen came out of the jet, impinged on the platinum and ignited; the flame so produced could be used for lighting fires. Automatic gas lighters based on the same principle have been on the market in recent years; they contain a small amount of finely divided platinum which, when held over the gas jet, stimulates a catalytic reaction, between the hydrogen in the coal-gas and the oxygen of the air, of sufficient intensity to cause the gas to inflame. Unfortunately the impurities in the gas gradually deprive the catalyst of its activity and we then say that the catalyst is 'poisoned'.

In the course of the development of chemistry very many examples of catalysis were discovered, and we now know that it is a fairly general phenomenon; a large number of catalytic actions, as we shall soon see, have important industrial applications. No universal catalyst has yet been found which will speed up every reaction; as a general rule each process requires its own special catalyst, and so far we have been able to make very little progress in the correlation of the nature of the chemical reaction with that of the substance by which it is catalyzed. One of the most important characteristics of catalysis is that the catalyst itself is not used up in the chemical action and so a very small quantity can stimulate very considerable changes.

Although the realization of catalytic action is comparatively recent, yet the acceleration of various processes by catalysts has been going on in Nature probably ever since living things first existed. We have already seen in our discussion of the digestion of food that various parts of the body produce a number of juices which help to decompose the carbohydrates,

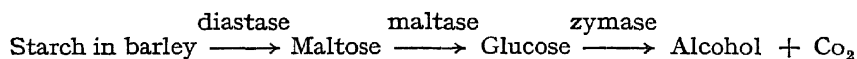
proteins and fats ; it is only in recent years, however, that this knowledge has been obtained and it has been gradually realized that these juices contain a number of different catalysts. At one time it was thought that digestion was a process of putrefaction, or rotting, which was associated with the living organism and could not occur in its absence, but in the course of various investigations it was found that gastric juice even when removed from the stomach could still bring about the decomposition of proteins, whilst saliva, even though it contained no living matter, when placed in a glass vessel could still convert starch into maltose (p. 129). Similar decompositions could be brought about in the complete absence of any life products by means of a hot solution of hydrochloric acid ; in these reactions the acid acted as a catalyst, and hence it appeared that the digestive action of gastric juice, and of saliva, was due to different catalysts present in these secretions.

In 1896 Edward Büchner, of Wurzburg, published the results of a most important discovery which threw considerable light on the problem of chemical action in life processes ; he found that if yeast is ground down, so that the small cells of which it is composed are crushed and broken, and the resulting mixture is filtered, a liquid still having the power of converting sugar into carbon dioxide and alcohol can be obtained. This liquid contained no trace of any living organism, yet it had all the fermenting power of yeast. It appeared, therefore, that alcoholic fermentation and food digestion were not to be regarded as decompositions inseparable from life processes ; they are rather catalytic reactions stimulated by certain substances *produced* by living organisms, but which could still act as catalysts when removed from living matter. These catalytic agents are now called 'enzymes', from two Greek words meaning 'in yeast', and, except for the fact that they are rather complex chemical substances, they have exactly the same characteristics as inorganic catalysts derived from non-living sources. Owing to their very great complexity, it has not been found possible to prepare an enzyme in the laboratory without reference to a living organism, but this may well be one of the chemical triumphs of the distant future.

. A very large number of different enzymes have been detected ; each one of these can catalyze one reaction and



one reaction only. The enzymes of the digestive juices have already been dealt with at some length (Chap. XI), and so no further reference will be made to them here, but a few others will be discussed briefly. Yeast contains a large number of enzymes of which the three more important have been called 'zymase', 'invertase' and 'maltase'. The first of these stimulates the decomposition of the simple sugar glucose into alcohol and carbon dioxide; whilst the latter two aid the conversion of the di-saccharides, sucrose and maltose, respectively, into glucose, etc. (p. 129). Yeast, therefore, is able to ferment more complex sugars as well as the simpler one, but in the pure state it cannot ferment starch. An enzyme is first required which will convert starch into a simpler sugar, and such an enzyme is actually present in malt obtained from germinating barley; it is known as 'diastase', and it accelerates the change from starch to maltose. The maltose can subsequently be converted into alcohol by means of maltase and zymase of yeast. In the production of beer from barley, the latter is allowed to germinate in order to produce diastase, which converts most of the starch present in the seeds into the sugar maltose; the mixture is then heated in order to destroy the enzyme and yeast added to complete the fermentation process. We may picture the process thus:



Rennet, used in the making of cheese, contains an enzyme 'rennin' produced in the stomach of the calf; this enzyme affects the protein, casein, present in milk and causes it to coagulate and form curd. It has been found that one part of rennet can coagulate over a quarter of a million times its own weight of casein from milk, and hence we have an excellent illustration of the statement made previously, that only a very small amount of catalyst is required to produce quite considerable changes. After the curd is drained and pressed it is allowed to 'ripen' in order to produce cheese; various complex changes occur which depend on the nature of the enzymes present, and it is on these changes that the flavour of the cheese depends. The presence of different enzymes will naturally result in the production of a different kind of cheese; these enzymes are produced by various micro-

organisms which may be present, or which are deliberately introduced.

It has been known for hundreds of years that wines are liable to become sour if exposed to air; we now know that this is due to an oxidation process catalyzed by an enzyme produced by certain moulds and bacteria. Some of the organisms producing this enzyme are generally present in air, but in the manufacture of malt vinegar the fermented barley is inoculated with the 'acetic acid bacteria' so that the oxidation process can occur readily. One other enzyme catalyst of the very many which play an important part in common phenomena of daily life is worth mentioning. It is produced by the lactic acid bacillus and converts the lactose (milk-sugar) present in milk into the sour lactic acid; hence it is responsible for the souring of milk. It is interesting to note, too, that the production of cold light by various living creatures, such as the fire-fly for example, is connected with the presence of an enzyme.

An interesting recent application of enzyme action to industrial chemistry was made in connexion with the discovery of a bacterium which had the capacity of aiding the conversion of carbohydrates into butyl alcohol and acetone. These two substances were originally required for use in a method suggested for making artificial rubber, and the anticipated demand for this purpose stimulated the perfection of this catalytic process. During the war large quantities of acetone were required for the production of cordite, and the ordinary sources, such as wood distillation (p. 177) were unable to meet the demand; the fermentation of maize by the special acetone-producing bacteria was then carried out on a large scale. At the present time both acetone and butyl alcohol are used very considerably in the manufacture of solvents, and they are made to some extent by this method, particularly in the United States.

Enzymes not only have the power of decomposing various complex substances into simpler materials, but they all possess, to some degree, the power of re-building the complex from the simple substances under appropriate conditions. Up to the present very little attention appears to have been paid to this aspect of enzyme action, but there is every possibility that in the future the chemist will call to his aid catalysts made by living organisms, in his attempts to synthesize in

the laboratory and in the works comparatively complicated materials from simpler ones.

- Although the natural or organic catalysts—the enzymes—play a very important part in fermentation industries, yet the artificial or inorganic catalysts, which the chemist has devised play an even greater rôle in many manufacturing processes. Let us consider in the first place sulphuric acid, one of the most important of the chemicals used in industry ; the world's production of this acid is about 10 million tons per annum. Nearly half of this is used in the manufacture of calcium superphosphate manure, about which more will be said later (Chap. XIV), whilst about another 30 per cent. is required for making sulphate of ammonia, a valuable source of nitrogen for soils. A certain amount of sulphuric acid is also used in the manufacture of dyes, explosives, hydrochloric and nitric acids, and in petroleum refining, as well as to a minor extent in many other industries. All this sulphuric acid is made by one of two catalytic processes ; in the older method known as the 'lead chamber' process the catalyst is a gas called nitric oxide, whilst in the newer method, called the 'contact' process, the catalyst is usually a finely divided form of platinum. In each case the gases oxygen ( $O$ ) and sulphur dioxide ( $SO_2$ ), which only unite together very slowly under ordinary conditions, are made to combine with considerable speed in the presence of the catalyst ; sulphur trioxide ( $SO_3$ ) results, and this is absorbed in water by suitable means to form sulphuric acid ( $H_2SO_4$ ). The development of these catalytic processes has reduced the price of the acid from about thirteen shillings per pound in the middle of the eighteenth century, to about a halfpenny per pound to-day.

The conversion of liquid oils to solid fats has been one of the recent achievements of chemistry ; the process is a catalytic one, involving the use of hydrogen gas, and is generally known as the 'hardening of fats'. The chief liquid fats are whale and fish oils, and various vegetable oils such as cottonseed, soya bean, ground nut, palm kernel, sesame and olive oils ; these are cheap and plentiful, but they had very little commercial value until a method was discovered for converting them into solid fats useful for making soap, lubricants, candles and also for the artificial lard used in the United States and on the continent of Europe for confectionery and biscuit making. All fats, both soft and hard, are glycerine

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compounds of fatty acids (p. 133), the only difference between them being that in the case of the hard fats more hydrogen is present than in the soft ; if we could add hydrogen, therefore, to the molecule of a soft fat we ought to obtain a hard variety. If hydrogen gas is just bubbled through a liquid oil apparently nothing occurs, but in the presence of a catalyst the union between the soft fat and the hydrogen can take place quite readily, and a hard fat results. The catalyst invariably used in technical practice is the metal nickel in a very finely divided condition ; only a small amount of this catalyst is required for the hardening of a large amount of oil. In actual practice the nickel is suspended in 300 to 500 times its own weight of oil heated to about  $180^{\circ}\text{C}$ . and pure hydrogen gas at a pressure of roughly 25 pounds to the square inch is passed in. When the oil has taken up about 1 per cent. of its weight of hydrogen it will have the consistency of lard on cooling, although it actually contains only about one-eighth of solid fat ; thus 1 ton of cotton-seed oil requires about 1,500 cubic feet of hydrogen in order to produce a solid fat of definite commercial value. Since this process for the hydrogenation of fats was first worked on an industrial scale at Warrington in 1910, over 500 patents have been taken out dealing with improvements of technical details, and now the hardening of oils is an important industry ; at least 500 million pounds of oil are treated annually by this process in various parts of the world.

Catalysts play a very important part in two aspects of chemistry which are the most likely to show considerable developments in the near future ; these are the production of artificial manures and of petrol substitutes. We shall see later (Chap. XIV) that the shortage of natural fertilizers and an ever-increasing food requirement for an ever-expanding population have compelled chemists to devise methods of fixing the free nitrogen gas present in the air into some chemical combination which the plant can use ; in several of these processes catalysts are essential and in general the most successful manufacturers are those who have discovered the best catalysts. The nature of these is so important that they are usually kept a strict secret. When discussing the requirements of plants we will consider the methods of nitrogen fixation in more detail (p. 169). In the other aspect of chemical development—the production of artificial liquid fuels

—catalysis is destined to play a part. The internal combustion or petrol engine is a most convenient power unit, but the supply of petrol is not inexhaustible ; methods are, therefore, being devised for the production of a liquid fuel from ' water-gas ' by passing it over a catalyst under suitable conditions. The nature of the resultant compounds varies very greatly with the nature of the catalyst and many investigations are being carried on to discover the most suitable one (p. 198).

Before concluding this section on catalysis reference must be made to one of the great romances of chemistry in which a catalyst played a great part. In the course of the experimental work carried out in Germany at the end of the last century with the object of making synthetic indigo, a substance known as phthalic acid was required on a large scale. This material was expensive and difficult to make, but its chemical relationship to naphthalene, obtained from coal tar, was well known, and so it appeared that phthalic acid might be made from cheap naphthalene. At first the results were unsatisfactory, but on one occasion when the raw material was being heated with strong sulphuric acid a thermometer used for measuring the temperature was broken by accident, and some mercury ran into the reacting mixture. Immediately a vigorous action commenced, and in a short time the naphthalene had changed to a mass of phthalic acid ; mercury was just the catalyst required to make this particular change occur with reasonable speed. The production of cheap phthalic acid made the synthetic indigo industry possible, and in the course of years it has almost completely displaced the production of natural indigo (p. 221) ; in any case indigo is much cheaper and a more uniform dye than it was thirty years ago. No doubt synthetic indigo would have become a commercial article even if the mercury catalyst for the production of phthalic acid had not been discovered, but the development of the industry would have been delayed many years. At the present time an even better catalytic process has been developed, and the naphthalene is oxidized to phthalic acid by the oxygen of the air.

There is probably a very great future for catalysis and even now we cannot realize fully the results that may yet be obtained, in various directions, by the discovery of suitable catalysts. One of the dreams of scientists is to produce a source of cold light, since this would be far more economical

than any known method of illumination ; we know that the fire-fly can do this by means of an enzyme catalyst and it is only a matter of time before the chemist will imitate the process.

#### QUESTIONS

1. What is meant by catalysis ?
2. Give some examples of reactions in which (a) natural, and (b) artificial catalysts are involved.
3. What is Döbereiner's lamp ? How does it illustrate catalytic action ?
4. What are the functions of malt and yeast in the fermentation of barley ?

#### SUBJECTS FOR ESSAYS AND DISCUSSION

1. Enzymes and catalysis.
2. The importance of inorganic catalysts to industry.
3. The industrial importance of enzyme actions.
4. The relation of enzymes to life processes and living organisms.

#### FURTHER STUDY

1. Future developments in catalysis.
2. The possibility of producing cold light.
3. The mechanism of enzyme action.
4. Enzymes as catalysts for synthetic processes.

#### BOOKS TO READ

Chemical Discovery and Invention in the Twentieth Century. Tilden. (Routledge.)  
The Romance of Chemistry. Foster. (Allen and Unwin.)  
The Chemistry of Commerce. Duncan. (Harper Bros.)  
Chemistry in the Service of Man. Findlay. (Longmans, Green.)  
Chemistry in Agriculture. (Chemical Foundation, New York.)  
Chemistry in Industry. Vol. II. (Chemical Foundation.)  
Industrial Applications of Catalysis. Jobling. (Churchill.)  
Catalysis in Theory and Practice. Rideal and Taylor. (Macmillan.)

#### SUGGESTIONS FOR EXPERIMENTS

Catalytic decomposition of hydrogen peroxide and potassium chlorate.

Acids as catalysts in hydrolytic reactions.

Production of diastase in barley during germination.

## CHAPTER XIV

### PLANTS AND THE SOIL

N EARLY all of our food material comes from the soil, either directly or indirectly, in the form of plants. When the world was not very thickly peopled and there was a large area of virgin, uncultivated land still available for the growth of crops the supply of food produced in the world was sufficient to meet the demand. In recent years, however, the human population of the earth has been increasing rapidly and it has been foreshadowed that unless the best possible use is made of agricultural land a serious food shortage is imminent. Fortunately the biologist and the chemist have been studying the problem and some useful results have already been obtained by determining the conditions under which different plants will grow best. Such information is clearly essential in order that the best results may be obtained from the limited amount of land available for food production.

Just over 300 years ago, Van Helmont (p. 75) made the first definite attempt to discover of what a plant was made. He planted a young willow branch weighing 5 pounds in a large earthenware vessel containing 200 pounds of dried earth. To this he added *only* pure water in the form of distilled water, or rain water, and in the course of five years Van Helmont found that the weight of the tree had increased to 169 pounds, whilst at the same time the earth in which it was planted had only lost 2 ounces in weight. This remarkable experiment appeared to prove quite conclusively, as Van Helmont said, that 'the one hundred and sixty-four pounds of wood, bark and roots by which the older tree differed in weight from the younger one, were therefore derived from water alone'. Unfortunately this apparently conclusive result was wrong. One factor—an extremely important one—had been neglected ;

Van Helmont had not taken into account the part that might be played by the gases present in the air ; this omission is all the more remarkable since, as we have already seen, it was he who first identified the very gas, carbon dioxide, which we know to be so important for the growth of a green plant (p. 101). Although the amount of carbon dioxide in the air is comparatively small, only three to four parts per 10,000, yet owing to the wonderful balance of Nature it keeps remarkably constant, and being continuously present plants evidently find it sufficient for reasonable growth.

Experiments have been tried to determine the effect of increasing the amount of carbon dioxide available for the plant ; it has been claimed that up to a certain point this increase has been beneficial and a more rapid growth has resulted. It is possible that waste carbon-dioxide gas from breweries, bakeries and chemical works may be utilized to stimulate the growth of plants—especially in an enclosed space like a greenhouse—but the most hopeful development in this connexion would be the discovery of a substance which could be placed in the soil and which would liberate a continuous supply of carbon dioxide for the use of the plant. As the gas is only required in sunlight perhaps we could make use of the sun to cause the substance to set the carbon dioxide free ; let us hope that some scientist will solve this problem in the near future. Attempts have also been made to increase the working day of a plant beyond the hours permitted by the sun ; in other words, artificial lighting, equivalent as far as plants are concerned to sunlight, has been turned on at sunset. It has been found that a tomato plant will continue to grow in the artificial light, provided that it gets at least five hours' rest in the dark per day ; if attempts are made to expose such a plant to light for more than nineteen hours a day it will wither away completely. Experimental work of this kind is only in its infancy, but the results may have an important bearing on the great problem of food supply.

Although carbon, hydrogen and oxygen obtained from carbon dioxide and water are the main requirements of plant life, yet the presence of small quantities of other elements in the soil have been found to be essential for normal growth and development to occur. Of these the most important are nitrogen, phosphorus and potassium, whilst small amounts



of sulphur, iron, calcium and magnesium must also be present. As a result of growing crops on a piece of land for several successive years, the soil is no longer able to supply sufficient amounts of the essential elements for normal plant growth; rain water also dissolves away some of the nutrient material present in the earth, and so the soil becomes infertile or barren. It has been known for thousands of years—the origin of the knowledge is lost in the mists of antiquity—that the fertility of the land for agricultural purposes could be greatly increased by applying farmyard manure to the soil, and this procedure was almost universally adopted by farmers. For a long time it was thought that the plant lived on the decaying *organic* vegetable matter of the manure, but towards the middle of the last century it began to be realized that the chief function of this material was to supply the *inorganic* salts, not obtainable from the air, which the previous crops had removed from the soil. This new idea was put forward by the German chemist Liebig in 1840; he claimed that if farmyard manure were heated in order to drive off all the organic matter, then the residual ash was as efficient a fertilizer as the original substance. After analysing the ash to find out what substances were present, it was possible to make up an exactly equivalent chemical manure without using any farmyard refuse. Examination showed that this ash contained no nitrogen, and Liebig was of the opinion that this essential element could be obtained by the plant from the air in the form of ammonia.

The important work of John (later Sir John) Lawes and Dr. (later Sir) Henry Gilbert, which was commenced at Rothamsted in 1843 and is still being carried on by others to-day, indicated that Liebig was probably not quite correct. With many crops the addition of the ash of farmyard manure only, resulted in no improvement in the plant growth, but the addition of sulphate of ammonia to the ash produced a marked increase in the yield of the crop. It is clear, therefore, that many plants are unable to utilize the nitrogen from the air, but must have it supplied in a combined form; the original farmyard manure contained some nitrogen in this form, but it was driven off, together with the organic matter, in producing the ash. In the middle of the last century, no doubt as a result of the 'swing of the pendulum' many scientists thought that the organic matter in farmyard refuse

had no influence on plant growth, but we shall see later that this view is not quite correct.

In order to maintain the fertility of the soil, it is clearly necessary to return to it just as much as the plant crop has removed; at one time this could be achieved by the application of farmyard and household refuse, but in recent years, as a result of the concentration of the population in towns, the decreased use of animals on farms, and the increased area of cultivation the amount of refuse available is not nearly sufficient to supply the requirements of the soil. Chemists have, therefore, attempted to supplement, or even replace, the natural fertilizer by means of artificial manures obtained from mineral and other sources. The elements which have generally to be added to the soil in the largest amounts are nitrogen, potassium and phosphorus, but these must be present in some 'available' form in which the plant can make use of them. It has already been mentioned that the plant obtains its food from the soil in the form of a solution, and hence the artificial manures must be soluble to some extent in water; if they are too soluble, however, they are liable to be washed away by rain.

Of the three important elements mentioned nitrogen should be considered first, because, as a rule, its compounds are more readily washed out of the soil than those of the other elements, and so they require most frequent replacement. As a matter of fact about 5 pounds of nitrogen per annum are added, on the average, to every acre of soil by the rain, but a much larger amount is dissolved away. Although there are twenty million tons of nitrogen gas over every square mile of the earth's surface, unfortunately very few plants are able to make use of the element in its free and uncombined state. Only leguminous plants, such as peas, beans, clover

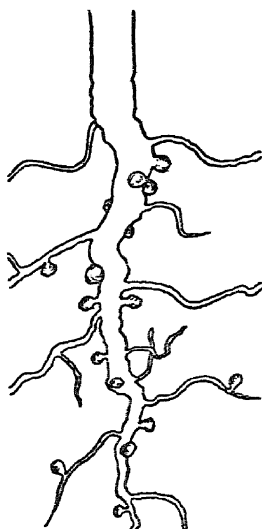


FIG. 17. — Root of Leguminous Plant showing Nodules, containing combined Nitrogen, produced by Micro-organisms

and lucerne, are able, by the aid of certain micro-organisms present in the soil, to utilize nitrogen from the air ; moreover, these plants are able to store extra nitrogen in an available combined form in certain nodules on their roots. Hence one way of adding nitrogen to the soil is to grow a legume and, after reaping the crop, to plough the roots well into the ground so as to provide nitrogenous material for other plants. In the process of rotation of crops it is generally recommended that lucerne be grown one year ; enough nitrogen is stored up in this way to last at least for five successive crops of roots and cereals.

In many cases, however, especially where intensive culture is necessary, it is more convenient for the farmer to apply his combined nitrogen in the form of an easily handled chemical manure. Since about 1860 the chief source of nitrogen for the soil was the 'nitrate of soda' which is found in South America ; in Chile there are vast natural deposits which, at the present rate of consumption, will probably last at least another century. Some years ago it was thought that these supplies of nitrate would soon be exhausted, and in 1898 Sir William Crookes, an eminent scientist, gave a very sensational address on the subject, at the British Association meeting ; he said that unless chemists devised methods for fixing some of the nitrogen of the air in a form in which plants could make use of it, we should soon be unable to grow enough wheat to feed the increasing population of the world. Although Sir William Crookes' alarm was rather premature, yet our almost complete dependence on Chile for the supplies of nitrate required not only for agricultural purposes but also for making nitric acid—essential in the production of explosives, dyestuffs, lacquers and some forms of artificial silk—is so unsatisfactory that methods are being developed for fixing the nitrogen of the air either in the form of nitrates or of ammonium salts. It should be mentioned that the plant, as a rule, uses its nitrogen in the form of nitrate, but there are generally present in the soil micro-organisms which have the power of converting ammonium salts into nitrates, so that either form may be supplied to the soil.

There are three main methods in use to-day for fixing atmospheric nitrogen ; in the oldest of these the nitrogen and oxygen of the air are made to unite together at a very high temperature—nearly  $3,000^{\circ}\text{C}$ .—produced by a large

electric arc. A compound of nitrogen and oxygen results which can readily be converted into nitric acid and nitrates. This method is only practicable where electricity can be obtained cheaply from water power and so cannot be made a commercial success in this country. The process was invented by two Norwegians, Birkeland and Eyde, in 1902, and it is still being worked in Norway, although it only accounts now for about 4 per cent. of the world's output of synthetic or fixed nitrogen compounds. Another method, which was devised by a German named Haber, is being developed to a large extent in Great Britain and other countries. A mixture of nitrogen and hydrogen, obtained from air, steam and coke (p. 53), is passed at 200 atmospheres pressure over a catalyst at a temperature of about  $550^{\circ}$  C. when ammonia gas ( $\text{NH}_3$ ) is produced. The actual nature of the catalyst used is not divulged, but it is believed to consist mainly of iron together with small amounts of other substances. The ammonia can be converted directly into sulphate of ammonia, an excellent nitrogenous fertilizer, or it may be oxidized to nitric acid and nitrates. In Great Britain it is estimated that during 1928 about 70,000 tons of nitrogen will be fixed as ammonium salts, or as nitrates, by this process; this is equivalent to about 280,000 tons of ammonium sulphate. The third process for fixing nitrogen is the cyanamide method, which is responsible for one-fifth of the world's total output; owing to the competition of the Haber process this proportion is likely to decrease in the future. In this method nitrogen from the air is passed over heated calcium carbide and a substance called calcium cyanamide results. This is sometimes used directly as a fertilizer under the name of 'nitrolim', but it may be converted into ammonium salts if desired. The world output of fixed nitrogen, which is already about 700,000 tons per annum, will certainly be increased in the near future, and so there is not likely to be any shortage for agricultural purposes, especially as the new methods of treating coal, for the production of gas and other smokeless fuels, will yield increasing amounts of by-product ammonium salts (p. 193).

Nitrogen is required by plants in order that they may synthesize amino-acids for the building up of proteins—an essential portion of the diet which we are unable to synthesize ourselves (p. 135). The addition of nitrogen to the soil promotes plant growth; it makes the leaves a vivid green and

causes a rapid growth of leaf and stem. It is stated that the addition of one hundredweight of ammonium sulphate to an acre of ground will result in an increased yield of 250 to 300 pounds of wheat, barley or oats, or 1 ton of potatoes, provided all other essentials are present. It is particularly useful in connexion with grassland cultivation. If the soil is starved of nitrogen the leaves are stunted and yellowish instead of green; an excess, on the other hand, produces coarse and rank growth, and there is a tendency for the plant to be attacked by fungoid diseases.

We will next consider the element phosphorus; this generally has to be applied in the form of phosphate, that is as a salt of phosphoric acid. For well over 100 years bones, which contain calcium phosphate, have been used in some form or another as an artificial manure. Originally the bones were broken up into roughly half-inch pieces, and buried in the ground; later it was found that better results could be obtained by grinding the bones to a fine powder—bone dust—or, better still, by steaming the bone dust to remove fats, gelatine and other impurities. This material was not quite satisfactory because it was only very slightly soluble in the water of the soil and so was not readily available for the plant. In 1842 John Lawes devised a process for acting on the calcium phosphate of bones with sulphuric acid, and so produced a substance generally known as 'superphosphate', which is more readily soluble in water and consequently acts on the plant more quickly than the untreated bone dust. At the present time superphosphate is generally manufactured from mineral phosphates, of which vast deposits have been found in North Africa and in the United States. A certain amount of phosphate manure is sold in the form of 'basic slag'; this is a by-product in one of the methods used for making steel from iron which contains a large proportion of phosphorus (p. 205). The excess of the latter is removed in the form of a phosphate slag. Experimental work is being carried out both in this country, and in Germany, with the object of manufacturing economically ammonium phosphate, which will supply both nitrogen and phosphorus to the soil; there is very little doubt that in a short time this commodity will be on the market as a practical fertilizer available on a large scale. The presence of phosphate in the soil improves root development, and hence it is very useful for swedes and

turnips ; it is also supposed to hasten the ripening of grain and so should be useful in cold and wet districts.

The third essential constituent potassium, often referred to in the form of its compounds as 'potash', is generally present in the soil to a very considerable extent but, unfortunately, in a condition in which it is not easily available for the plant. Potassium is present in a large number of rocks, and as these disintegrate, as a result of weathering and chemical action, the potassium finds its way into the soil ; it exists, however, in the form of insoluble compounds, such as felspar, from which the potassium is only removed very slowly. If a piece of land is to be used regularly for agricultural purposes potassium must generally be added, from time to time, in the form of a soluble salt, such as the sulphate or the chloride. The chief source of potash is the huge deposit of salts at Stassfurt in Saxony ; these minerals were discovered whilst a search was being made for common salt and were at one time regarded as useless. In 1861 it began to be realized that the crude material of these deposits could be utilized to provide potassium salts for agricultural purposes, and so a new industry has grown up—the mining of the Stassfurt deposits—which produces about 14 million tons of crude potash salts every year. The deposits are 5,000 feet thick in places and, at the present rate of utilization, appear to be almost inexhaustible ; they were most probably left behind by the sea as a result of successive inroads made over a period of about 10,000 years. Until recently Germany had almost the complete monopoly of the world's potash supplies, but since 1919 the deposits in Alsace, which now provide 30 per cent. of the total potash output, have been in the hands of France.

During the war efforts were made both in this country, and in the United States, to obtain local supplies of potash when the German material was not available ; small quantities were scraped together from seaweed, sugar-beet wastes, wood ashes and from blast furnace and cement flue dust, but the total was not nearly sufficient to supply the full demands of the soil. Most countries are, therefore, dependent on France and Germany for their potassium salts. Two factors might relieve the situation in the future ; the first may soon be in actual operation, but the second is more remote. The salt lakes, like the Dead Sea in Palestine, and Searles Lake

in California, contain potassium salts together with many other substances, and methods are being developed for the extraction of the potassium compounds; although the process of purification is feasible it is not yet certain that it is an economic proposition. The other possibility is that potassium might be extracted from granite and other rocks; there is an almost unlimited supply of potash in this country locked up in such substances, but it is not readily available. The day may soon come, however, when a simple chemical method is discovered for extracting the potassium in a soluble form.

The presence of potash in the soil favours the formation of carbohydrates, that is sugar and starch, and so it is desirable when growing sugar-beet, mangolds and potatoes. Potassium increases the resistance of plants to disease, and it has recently been stated that it is especially useful under unfavourable weather conditions when it can largely counteract the want of sunshine. In a country like England, therefore, both potash and phosphate fertilizers should be particularly useful in overcoming the disadvantages of bad weather.

There is a growing tendency at the present time to manufacture mixed fertilizers which contain nitrogen, phosphorus and potassium; an example of this type is 'nitrophoska', which is being made in Germany. These mixtures are imitations of the natural 'guano', found on islands off South America, which had such a tremendous vogue as a manure that the supplies were almost completely exhausted many years ago. Unfortunately not all crops require similar proportions of the three important elements, neither do all soils require the same treatment, hence there will always be a demand for the simple fertilizers like nitrate of soda, sulphate of ammonia, superphosphate of lime, and sulphate of potash. Grain crops as a rule require little potassium whilst roots require more, and hence in the rotation of crops it is usual to alternate a grain crop with potatoes, mangolds or beet; this perfectly sound system was discovered empirically long before the explanation was known! The alternation not only helps to keep the soil in good condition, but it also prevents the complete exhaustion of any important constituent.

In addition to the three elements which must be replaced in the soil fairly frequently the element calcium is often applied, although it is rarely deficient. It is generally added, at intervals, in the form of lime, or limestone, in order to

neutralize the acidity of a 'sour' soil. Most plants do not thrive in an acid soil—rye and potatoes are possible exceptions—and so this condition must be avoided. The use of sulphate of ammonia as a source of nitrogen encourages acidity, whilst nitrate of soda tends to make the soil alkaline and so the latter should be used on an acid soil; too much alkali, however, is just as harmful as too much acid. The addition of lime to a soil improves the texture by disintegrating the clay, and so it prevents stickiness. Some writers consider that the regular addition of lime to a soil improves the land in many ways, but at the same time the growth of weeds and insect pests is also encouraged. Lime must, therefore, be used with caution, and it gives excellent results with careful management. Magnesium, iron and sulphur are only required in very small amounts and these are never deficient; the first of these is present in chlorophyll, whilst the second, although not actually present, stimulates its formation. Sulphur is required for protein formation, but only in small amounts which are easily obtainable.

The elements already mentioned are those known definitely to be essential for plant growth, but in addition it is possible that very minute traces of certain other elements have some influence. Experimental work is being done on the effect of traces of boron, manganese, aluminium and of other elements in the soil, on plant development, but it is too soon yet to draw any definite conclusions. It is conceivable that the normal growth of a plant may require the presence of the merest traces of certain substances which play the same part in vegetable life as vitamins do in animal life. Some botanists have suggested that substances known as 'auximones' can be extracted from peat, and they have the power of stimulating plant growth; there is, however, no uniformity of opinion on this matter. We must wait patiently, therefore, for further information on the influence of traces of different materials on the growth of the plant.

It may well be asked if artificial chemical manures, containing all the required elements, are a complete substitute for natural farmyard refuse. In this connexion the experiments of Lawes and Gilbert, started in 1843 and carried on continuously at Rothamsted, have given interesting information. It appears that the plots on which natural manure has been used gave very regular yields and no signs of deteriora-



tion after eighty years of continuous cropping, whereas from those to which artificial fertilizer was applied less regular yields have been obtained, and there are indications of deterioration. It is possible that the natural manure may contain traces of certain substances which are able to stimulate plant growth, as indicated above, and about which we know nothing. It is known, however, that an important function of farmyard manure is to provide vegetable refuse in a form which readily disintegrates in the soil producing a dark brown organic material called 'humus'. This humus greatly improves the texture of the soil as it allows a better circulation of air, and also prevents the valuable soil solution from draining away too rapidly. Many farmers grow a green crop for the special purpose of ploughing into the soil so that it may be rotted away by micro-organisms and produce valuable humus. It is widely known that leaf-mould is a very suitable medium for plant growth; this is chiefly because it is exceptionally rich in humus produced by decomposition of the leaves. Attempts are now being made to produce a sort of artificial 'natural manure' by decomposing straw. In the ordinary way decomposition through the agency of soil bacteria is a slow process but a method has been devised to accelerate it; a nutrient medium is added to the straw and so the number and activity of the bacteria is greatly increased and decomposition into humus occurs rapidly.

There is very little doubt, therefore, that the chemist has already accomplished a great deal in helping the farmer in the intensive production of food, necessitated by the great increase in the population of the world and the concentration of people in large towns. The artificial chemical manure is much easier to handle than the natural material, since a dressing of 4 to 6 cwt. of artificials, the quantity generally applied to an acre of land, is equivalent to 10 to 14 tons of farmyard refuse. The latter is of uncertain composition whilst the former can be made up from various constituents according to the requirements of the particular soil and the crop to be grown. There are still a number of problems, however, for the future and one of the most important of these is to attempt to overcome the results of bad weather.

## QUESTIONS

1. Which elements are essential for plant growth?
2. Why did Van Helmont consider that a plant was composed almost entirely of water?
3. What is humus? How is it formed, and why is it useful to the soil?
4. Why are manures necessary? Trace the development in their use.

## SUBJECTS FOR ESSAYS AND DISCUSSION

1. The fixation of atmospheric nitrogen for artificial fertilizers.
2. Potash supplies.
3. The importance of leguminous plants in the rotation of crops.
4. The influence of nitrogen, phosphorus and potassium on plant growth and development.

## FURTHER STUDY

1. The possibilities of stimulating plant growth artificially.
2. Natural versus artificial manures.
3. Intensive grassland cultivation.
4. The physical properties of the soil.

## BOOKS TO READ

- Soil Conditions and Plant Growth. Russell. (Longmans, Green.)  
An Introduction to the Scientific Study of the Soil. Comber.  
(Arnold.)  
Creative Chemistry. Slosson. (Univ. of London Press.)  
Chemistry in Agriculture. (Chemical Foundation, New York.)  
Chemistry in Industry. Vol. I. (Chemical Foundation.)  
Chemical Discovery and Invention in the Twentieth Century.  
Tilden. (Routledge.)  
Chemistry in the World's Work. Howe. (Chapman and Hall.)

## SUGGESTIONS FOR EXPERIMENTS

- Examine the effects of various elements on a plant grown in sand,  
or in water.  
Test soil for nitrogen, potassium and phosphate.  
Test the acidity of soil and the neutralizing power of lime.  
Examine the nodules on the roots of leguminous plants.

## CHAPTER XV

### FUELS AND THEIR USES : WOOD AND PETROLEUM

WOOD, petroleum and coal are not only our chief sources of fuel, but they also form the raw materials for the production of a number of valuable substances useful in our daily lives ; in the present section an account will be given of some of these substances, and the processes by which they are obtained. For the sake of convenience it is proposed to discuss the applications and treatment of the three raw materials in the order given at the head of this paragraph ; wood and oil will be dealt with in this chapter, and coal in the next.

Most woods consist mainly of a kind of cellulose, which is a complex carbohydrate (p. 129), and a certain amount of plant juice, or sap ; the latter contains in solution various substances which act as food material for the tree whence the wood was obtained. At one time wood formed almost the only available fuel and it was simply burnt without any previous treatment, except drying. In due course it was discovered that charcoal, obtained by the partial burning of wood, was a more convenient fuel than wood itself, probably because it burnt more slowly and gave off less smoke ; even to-day charcoal is still used as a fuel in countries where wood is cheap and plentiful. The old method of carbonizing wood, as the process of charcoal making is called, was to make a large circular dome-shaped heap of logs and to cover it with a layer of clay and turf to prevent easy access of air. The heap was then set on fire in the centre and in the limited amount of air available only partial combustion occurred ; the heat drove off the volatile matter and left the charcoal behind. This method is still adopted in districts where the charcoal is the main requirement, but a newer process of carbonization has been devised resulting in the saving of valuable volatile substances which are otherwise wasted.

In the new method the wood is loaded into small cars which are run into large retorts, and there heated out of contact with air. The vapours coming off are condensed by cooling and the resulting liquid collected; charcoal remains behind in the cars and is readily removed. The liquid is allowed to stand and two layers—a lower tarry layer and an upper watery one—are formed; these are then separated from one another. The clear upper layer is distilled and two portions collected; the

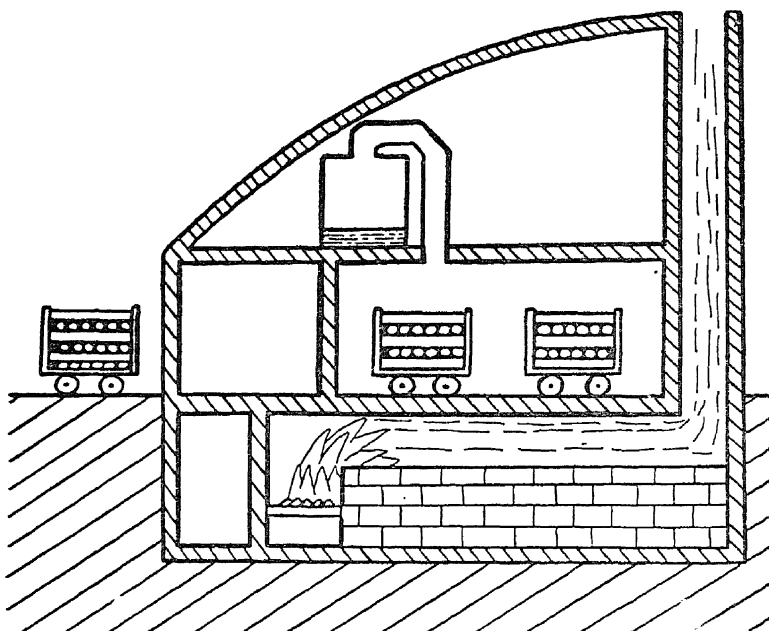


FIG. 18.—Diagram of a modern Charcoal-burning, or Wood-distillation, Retort

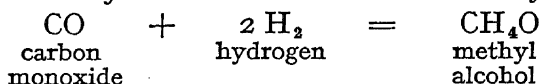
lower boiling-point fraction, called 'wood naphtha', contains chiefly methyl alcohol, acetone and methyl acetate, whilst the other is known as 'wood vinegar' and is a weak solution of acetic acid. Further purification of the naphtha yields almost pure methyl alcohol, and also a mixture known as 'methyl acetone' which is used as a paint remover. The acetic acid in the wood vinegar is generally neutralized by means of lime when the salt calcium acetate results; on evaporating the solution more methyl alcohol and acetone distil off, and even-

tually the solid salt remains. If this calcium acetate is heated either with hydrochloric or with sulphuric acid, a reasonably pure form of acetic acid is obtained; for special purposes this is generally purified further. On the other hand by heating calcium acetate alone the important solvent 'acetone' may be obtained.

The amounts of methyl alcohol and acetic acid obtained by the carbonization of wood vary with the nature of the latter, and with the method of heating. In general hard woods, such as oak, beech and maple, are used for carbonization, as they produce more of these products than do soft or resinous woods; but the latter—for example, yellow pine and Douglas fir—are often used for the production of resins and oils not obtainable from hard woods. The tarry layer of distillate, obtained when wood is heated, is sometimes distilled further when it yields oils used for creosoting and as insecticides and disinfectants, whilst the pitch left behind has valuable properties as an electrical insulator.

The three chief liquid products of wood distillation—namely, methyl alcohol, acetic acid and acetone—are substances of great industrial importance. The first of them is used in the production of dyes, perfumes, drugs and other chemical substances, whilst oxidation by air in the presence of copper as a catalyst yields formaldehyde (or formalin). This is an excellent germicide and also plays an important part in the manufacture of artificial resins such as 'bakelite'. Until recently methyl alcohol was obtained entirely by the distillation of wood, but in the last year or two a synthetic process has reached the stage of commercial production and promises to have a very great effect on the wood distillation industry. The raw material for this new method, which is being worked to a rapidly increasing extent in England, the United States, Germany, France and Italy, is coke; this is first converted by means of steam into water gas. By suitable treatment the proportion of hydrogen to carbon monoxide in the gas mixture is increased, and it is then passed at a pressure of about 150 to 200 atmospheres over a catalyst at 300° to 400° C. The nature of the catalyst is very important, because the products obtained vary considerably with different catalytic agents, as we shall see later; a combination of oxides is generally used for this purpose, and although the exact nature of these is kept secret, it is probable that mixed, or combined, zinc and chromium

oxides make a satisfactory catalyst. For the production of methyl alcohol by this method the reaction may be written :



Efforts are still being made to discover better catalysts and to improve the process and so reduce the cost of the methyl alcohol ; as it happens the technique involved is almost the same as that used in the manufacture of synthetic ammonia from the nitrogen of the air (p. 169), and the great improvements being made in the latter industry are certain to have an important influence on the production of methyl alcohol. There is very little doubt that in the near future, as a result of these developments and of the shortage of wood, almost the whole world supply of methyl alcohol will be of synthetic origin.

Acetic acid in various forms is an invaluable industrial product ; as vinegar it is used in the home for the preservation and pickling of various foods. It is chiefly used on the large scale in the manufacture of dyestuffs, flavouring essences and drugs, and of an important kind of artificial silk (p. 242). Acetic acid is also utilized to some extent in the production of pigments, white and green chiefly, in the preparation of lacquer solvents (p. 21) and for the coagulation of rubber. In addition to the acetic acid made from wood, some has always been prepared by the oxidation of alcohol in the presence of certain micro-organisms (p. 159) ; this method generally yields a weak solution of the acid and is used for table vinegar. During the war the process for the production of acetic acid from acetylene (p. 90) was developed in order to provide the acetone required in the manufacture of the explosive cordite, but the increasing demand for acetic acid itself since 1918 has resulted in the continued growth of this industry. Large quantities of synthetic acetic acid and its products are now manufactured in Canada and in Germany. Calcium acetate is one of these products and it is used in the preparation of acetone ; a certain amount of the latter substance is also produced by the fermentation of maize (p. 159). The chief use of acetone at the present time is in connexion with the storage of acetylene in cylinders for purposes of transport (p. 90), but some is also used for other solvent purposes ; acetone may possibly become one of the raw materials in the preparation of synthetic rubber, but this development may take many years. The greatly increased

demand for paper has resulted in a decrease of the amount of wood available for carbonization purposes, but fortunately, as we can see, the chemist has devised methods for the production of the three important products of wood distillation from other sources.

The manufacture of paper is probably the most important industry of to-day for which wood is a raw material. Although not all paper is made from wood, yet almost all the newspaper and book paper, and a good deal of writing paper, does originate from it ; in addition, cotton, linen rags, straw and esparto grass are used to some extent for paper production. The wood is first disintegrated into small shreds known as ' pulp ' ; this may either be done mechanically by grinding in machines, or else by chemical disintegrating materials. The former process generally yields an inferior grade of paper. The most important chemical method for producing pulp is to boil the wood shavings, or chips, with calcium bisulphite solution under pressure ; in other processes the wood is heated with caustic soda alone or with a mixture of this and sodium sulphide. The fibres are washed to remove the chemicals, then they are passed through screens to remove knots, unchanged wood and impurities, and finally bleached by chlorine or ' bleaching powder '. The bleached fibres are ' beaten ' to cause them to disintegrate further and then they are in the right condition for paper-making. At this point various materials are incorporated into the pulp ; dyestuffs are added if coloured paper is desired, and then various substances, such as barium sulphate (barytes), precipitated chalk, china clay, starch or glue, known as ' loading ' materials are put in. These latter help to fill up the pores of the paper and allow a better glaze to be given to it in its final treatment. Paper made from the resulting pulp would be porous like blotting paper, and hence it must be ' sized ' in order to prevent ink spreading ; this is generally accomplished by adding rosin soap, made by treating rosin with alkali, and alum. The pulp and water are now run through fine wire-cloth screens which retain the fibres and allow the liquid to drain away ; the continuous thin layer of pulp is pressed between rollers to expel water. Finally the paper so formed is ' calendered ', that is it is pressed between hot metal rollers, in order to impart a smooth surface. The draining, drying and calendering are generally carried out as a continuous process by machinery.

For special papers special methods of treatment are used various stages of the manufacture. Blotting paper is unsized paper, whilst parchment paper is generally made by dipping an unfilled and unsized paper into fairly strong sulphuric acid ; a chemical action between the acid and the cellulose results in the production of a gelatinous sizing material which fills the pores of the paper and makes it strong, translucent and non-porous.

Wood is also utilized to a considerable extent in the manufacture of artificial silk (p. 240) as well as for nitrocellulose which is used as an explosive and in the production of lacquers (p. 114).

The term petroleum is derived from two words meaning 'rock oil' ; it is applied to an oily liquid, varying in colour from yellow to pale brown or even black, which either exudes from the earth or else is obtained in certain parts of the world by boring below the surface. Long before the commencement of the Christian era the Persian fire worshippers made their pilgrimages to the 'eternal fires' of Baku, which were fed by petroleum and by gases associated with it ; later, during his voyages in the East, made in the thirteenth century, Marco Polo, the famous traveller, described the springs of 'oil not good to use with food, but good to burn and also to anoint camels'. For many years crude petroleum was used as a sort of lubricant to ease the backs of beasts of burden, whilst the North American Indians used it as a medicine. In 1849 a druggist in Pittsburgh, U.S.A., collected oil from a brine well and sold it as a 'natural remedy, celebrated for its wonderful curative powers' ; even to-day we use 'liquid paraffin', a purified petroleum product, as a laxative, but eighty years ago the crude material was regarded as a cure for all ills. Undoubtedly it had a beneficial effect because there was a considerable demand for the medicine, and in 1854 the Pennsylvania Rock Oil Company was formed to develop petroleum production for this and other purposes.

In 1859 the first oil well was dug and petroleum was reached 70 feet below the surface of the earth. At that time the possibility of using the oil as a fuel was not fully realized, but the American chemist Silliman found that if petroleum were distilled the fraction coming over between the temperatures of about 100° C. and 300° C. could be used for illuminating purposes. This discovery resulted in an increased demand for



petroleum and production was increased very considerably ; no use, however, was found for the considerable portion of the oil which distilled below  $100^{\circ}\text{C}$ . and above  $300^{\circ}\text{C}$ . Soon it was discovered that the oil boiling above  $300^{\circ}\text{C}$ . could be used as a lubricant, but there was no appreciable demand for the low boiling portion until the internal combustion engine was developed towards the end of the last century. The great and growing importance of the motor-car and aeroplane, both of which use this type of engine, has led to a tremendous increase in the demand for ' petrol ' or ' gasoline ' as the easily boiling fractions of petroleum are called ; at the present time at least 10,000 million gallons of petrol are used annually in the world and nearly all of this is obtained from crude petroleum. Hence the production and treatment of this oil has become one of the most important industries of to-day.

Crude petroleum consists entirely of a mixture of several hundred different hydrocarbons of varying complexity. We have already seen (p. 87) that thousands of compounds of carbon and hydrogen may exist and petroleum oils of different origin contain different types of hydrocarbons. Thus Pennsylvanian petroleum contains chiefly paraffins, whilst that from Burma and Ceylon consists of olefines ; oil from Baku and Galicia contains a series of hydrocarbons known as ' naphthenes '. Since the nature of petroleum varies in different places, it is obviously difficult to account in a simple manner for the existence of these underground stores of oil. Various theories have been put forward from time to time to explain the origin of petroleum ; the one most generally accepted at the present day is that oil is due to the decomposition of vegetable matter, fish and marine animals which died and were deposited at the bottom of the sea. This decaying matter, it is thought, became covered with mud, clay or sand and was subjected in this way not only to the action of micro-organisms but also to the pressure and the high temperature beneath the surface of the earth. In the course of ages petroleum was formed and this was either absorbed by the clay to form oil-shale or else pools of oil collected and were prevented from escaping by upper and lower layers of limestone or shale. By drilling through the earth's surface an outlet is provided through which the locked-up petroleum can escape, often with tremendous force ; successive pools of oil have been found in a series of layers down to a depth of  $1\frac{1}{2}$  miles, and these may be

tapped in succession. The oil at first gushes up with great violence, but later it has to be pumped up as the pressure decreases ; it is then sent long distances through pipes to be refined.

The first stage of the refining process consists in separating the hydrocarbons of the oil into a number of portions, or fractions, with different boiling ranges ; this is known as 'fractional distillation'. The petroleum is run into a large vessel, or still, in which it can be heated gradually ; the vapours coming off between certain definite ranges of temperature are condensed by cooling and so a series of liquid fractions are obtained. A small quantity of gas is obtained which cannot be condensed, and this may be used as a fuel for heating the stills. The first liquid fraction is the chief source of petrol, but it also contains a certain amount of naphtha used as a solvent in dry cleaning and in varnishing. The next fraction is kerosene, which, after further treatment for the removal of unpleasant smelling sulphur compounds and other undesirable substances, is used mainly for burning in lamps using wicks—the so-called paraffin lamps. When kerosene was the most valuable petroleum product there was a tendency to allow some of the more volatile first fraction to mix with it ; this resulted in the production of an explosive vapour in the lamp, and several serious accidents occurred. A law was therefore passed to prohibit the presence of low-boiling range fractions in kerosene used for lamps ; at the present time, however, such laws are quite unnecessary as the first fractions are much more valuable than the kerosene. In fact the tendency to-day is in the opposite direction, and attempts are made to include in petrol some of the second, less volatile, fraction ; this is undesirable since it is essential that a good petrol should form a vapour very easily.

The third distillation fraction obtained from petroleum is called 'gas oil' ; it is too thick, or viscous, to be used in paraffin lamps, but yet not thick enough to use as a lubricant. Until 1912 there was very little use for this oil, but in that year a practical method was devised, known as 'cracking', by means of which the high boiling oil could be converted to some extent into more volatile oils available for use in the petrol motor. The general method adopted is to heat the gas oil at a temperature of about 400° C. and at a pressure of roughly 100 pounds to the square inch. The more complex, higher boiling

point hydrocarbons are split up by this means, to a considerable extent, into simpler, lower boiling point compounds which can be used as petrol; the vapour passing off during cracking is condensed and the liquid mixed with the ordinary petrol fraction. There is some tendency at the present time to develop 'gas-phase' cracking as against the more common 'liquid-phase' method; the former gives poorer yields of gasoline, but it is of a better 'anti-knock' nature (p. 115). The importance of cracking in petroleum refining is so great that hundreds of patents have been taken out dealing with various aspects of the process and with improvements in technique. It is worth noting that probably more than half of the total petrol used to-day is obtained by cracking gas oils.

The fourth main fraction obtained from petroleum is generally a mixture of viscous liquid and of solid hydrocarbons; if this is chilled the latter separate out, and, after purification from adhering liquid, form paraffin wax. Vaseline is frequently obtained from this fraction, whilst the liquid oils are used for lubricating purposes. The residue left in the retort after the fourth fraction of the petroleum has been removed sometimes consists of bitumen, or artificial asphalte; it may be used in road making, or for the preparation of a waterproof roofing material. The actual nature of the end products of petroleum distillation depends on the kind of oil used; Pennsylvanian petroleum, for example, yields considerable amounts of paraffin-wax but no bitumen, whilst Californian oil produces bitumen but no paraffin-wax. Some oils, on the other hand, may yield both of these products. With a non-bituminous oil the distillation is continued until the residue in the retort is almost pure carbon, or coke, which can be used as a fuel for heating purposes.

The relative amounts of the various fractions obtained from petroleum depend very much on the source of the oil; a typical example, however, is quoted by Wendt for United States Mid-continent petroleum: 4 per cent. gas, 25 per cent. gasoline (petrol) and naphtha, 15 per cent. kerosene, 40 per cent. gas oil, 12 per cent. lubricating oil, paraffin-wax, etc., and 4 per cent. coke. The gasoline fraction is carefully purified to remove sulphur compounds which not only have unpleasant odours but would produce corrosive acids in the cylinder of an engine; certain coloured impurities and materials of a sticky nature, which are very undesirable in petrol, are also removed.

The petrol as actually sold is a mixture of various products ; it should contain a proportion of low boiling-point, readily volatile hydrocarbons in order to ensure easy starting of the engine, and a certain amount of less volatile, and more complex, substances to furnish power and mileage. For use in cold climates and in aeroplanes the petrol must contain a large fraction of volatile hydrocarbons ; these are obtained to an appreciable extent from the ' casing-head gas ', that is, from the gas which collects at the top of an oil well. This gas was at one time wasted, but as it is saturated with gasoline it is now treated so as to remove the latter which may be used to improve petrol. It has been stated that about 8 per cent. of the world's petrol supply is now obtained from casing-head gas.

Although there are enormous deposits of oil-shale in various parts of the world, for example in Canada, the United States and in Scotland, very little attempt has been made, except in Scotland, to work them up. These shales are saturated with oily material, but the expense of mining, crushing and heating a great deal of useless rock is too great for the process to compete, at present, with the other methods of extracting oils. Geologists consider that the world's resources of petroleum are very limited, and that unless some vast new oil fields are discovered the supply of this material, at the present rate of consumption, may be exhausted in about twenty years.<sup>1</sup> It is possible that when this exhaustion appears imminent it will be essential to develop the vast oil reserves existing in shale deposits.

In Scotland the shales have been worked, since 1850, mainly as a source of paraffin-wax for candle making. Candles were originally made by dipping wicks made of pith of the rush, or of cotton, into either molten tallow or beeswax ; thus two types of candles—tallow and wax candles—were made. About 1750 the wax known as spermaceti, obtained from the sperm whale, was used as a raw material ; the candles made from it gave a large, regular and very luminous flame, but unfortunately they were expensive. At the beginning of the last century ' stearine ' candles made from a mixture of fatty acids,

<sup>1</sup> Sir Richard Redmayne said : ' Even if we take into consideration the comparatively new and rich fields in Mexico, Mesopotamia and Turkestan the resources of natural mineral oil will not suffice for more than eighty to a hundred years ' (Samuel Coal Commission, 1925).

chiefly stearic acid, were introduced; the stearine was made by decomposing tallow with dilute acids or by superheated steam. The next advance in the candle industry was made in 1850, when paraffin wax, obtained from Scottish oil shale, was utilized chiefly in order to improve the stearine candles. To-day, however, paraffin wax is said to be the main candle material; about 5 to 10 per cent. of stearine is added to reduce the brittleness of the wax. It is reported that in Great Britain 40,000 tons of paraffin wax and 3,000 tons of stearine are used annually, at the present time, in the manufacture of candles; in spite of modern inventions, therefore, this is still a considerable industry and there is a great demand for paraffin wax.

#### QUESTIONS

1. How is wood treated for the production of (a) charcoal, and (b) liquid by-products?
2. What are the chief liquid products of the distillation of wood? For what purposes are they used?
3. What is petroleum? How may it have originated?
4. Explain the difference between paraffin oil and petrol.

#### SUBJECTS FOR ESSAYS AND DISCUSSION

1. The synthetic production of methyl alcohol, acetone and acetic acid.
2. An outline of the manufacture of paper.
3. The uses of petroleum products.
4. The refining of petroleum.

#### FURTHER STUDY

1. The importance of conserving our fuel supplies.
2. The manufacture of candles.
3. The distribution of the world's oil supplies.
4. The manufacture of different types of paper.

#### BOOKS TO READ

Everyman's Chemistry. Hendrick. (Univ. of London Press.)  
 Chemistry in Modern Life. Arrhenius. (Chapman & Hall.)  
 Chemistry in the World's Work. Howe. (Chapman & Hall.)  
 Outlines of Industrial Chemistry. Thorp and Lewis. (Macmillan.)  
 Industrial Chemistry. Vol. II. Rogers. (Constable.)  
 Industrial Organic Chemistry. Sadtler and Matos. (Lippincott.)  
 Chemistry in Industry. Vol. I. (Chemical Foundation, New York.)  
 Oil. Mitchell. (Pitman.)

#### SUGGESTIONS FOR EXPERIMENTS

Distillation of wood.  
 Preparation of acetone from acetic acid.  
 Examination of methyl alcohol, acetone and acetic acid.  
 Determination of flash point of petrol and paraffin.

## CHAPTER XVI

### FUELS AND THEIR USES: COAL AND ITS PRODUCTS

**I**T is fairly certain that coal has been known as a fuel in this country for at least 2,000 years, but owing to the absence of chimneys it produced a great deal of unpleasant smoke and hence it was not a popular material for fires. Even as late as the middle of the seventeenth century objection was made to the use of coal on account of the smell which it produced on burning! The invention of the steam engine and the coming of the Industrial Revolution resulted in a greatly increased demand for coal as a fuel for heating purposes; at the beginning of last century, too, the possibility of lighting towns by means of gas obtained when coal is heated began to be realized and the 'Coal Age' really commenced.

Coal is undoubtedly of vegetable origin; it was probably formed in this way. Millions of years ago abundant vegetation flourished on the flat, marshy lands bordering lakes and the mouths of rivers; these plants and trees grew and died and new vegetation arose which pushed the dead matter into the water. In the course of thousands of years the layer of dead and decaying vegetation gradually became thicker and thicker; in time these layers became covered with clay and sand as a result of movements of the earth's surface. The vegetable matter thus became pressed down into the earth by the ever-increasing weight of hardened clay and rock above it, and so eventually became subjected to volcanic heat. The effect of heat and pressure was to cause a decomposition of the vegetation first into peat, then into lignite and this gradually changed to ordinary coal and finally to anthracite. These four substances mark more or less definite stages in the transformation of plants into coal; the proportion of water present decreases from peat to anthracite, and so also does the percentage of volatile material in the dry residue.

Ordinary bituminous coal generally produces about 20 per cent. of volatile matter, but anthracite yields only about 5 per cent. ; an average coal after drying contains about 75 per cent. carbon, 5 per cent. hydrogen, 7 per cent. oxygen, 10 per cent. ash and some nitrogen and sulphur, whilst anthracite consists of roughly 92 per cent. carbon, 2 per cent. hydrogen, 2 per cent. oxygen and 3 per cent. ash.

Anthracite since it contains very little volatile matter is a smokeless fuel and burns almost without any flame (p. 96) ; it ignites slowly, but with a good supply of air it produces intense heat. This variety of coal is found chiefly in South Wales and in Pennsylvania, U.S.A., and its main use is for steam raising in ships' boilers. The most common kind of coal is the bituminous type ; about 1,000 million tons of this coal are mined all over the world each year. Great Britain produces nearly a quarter of the whole supply, whilst the United States provides about one half. By far the greater proportion of the bituminous coal used is burnt directly for the production of heat utilized for raising steam or for domestic purposes ; thus of the 180 million tons of coal which are consumed in this country every year, 40 million tons are burnt in domestic grates for heating and cooking, about 80 million tons are used for steam engines, etc., in general manufactures and in mining, roughly 16 million tons are required for railway engines and for coastal vessels, and 8 million tons are burnt in power stations for the production of electricity.

In the general method used for burning coal probably not more than half of the heating value of the coal is actually used ; the rest passes up the chimney to a great extent as waste heat, whilst a large proportion of the volatile matter is lost as smoke. It has been estimated that nearly 3 million tons of coal are wasted in Great Britain every year in the form of smoke ; in fact it was stated before the Samuel Coal Commission in 1925 that 'one million miners work three days every year to make soot to pollute the atmosphere'. Not only does this mean a tremendous wastage of a very valuable material, but the poisoning of the air by the coal-gases has a harmful effect on the health of the people living in large towns. Smoke can reduce very considerably the amount of ultra-violet light, coming from the sun, which is known to have definite health-giving properties. The acids present in soot and smoke also destroy vegetation, and cause brickwork and

mortar to be gradually worn away. It is stated that the total damage caused in London by smoke each year costs nearly £1 per head of the population, whilst in Manchester the total cost per annum is approximately £1,000,000, of which about one-quarter, it is estimated, is spent on extra laundry bills. If we could make every consumer of coal use a smokeless fuel, then we should not only save the coal wasted as smoke, and the cost of cleaning, but there would be no more black fogs, and the death rate from certain diseases would undoubtedly diminish. The problem is now to find some efficient, clean and economical method of utilizing our coal resources ; in this connexion there are several possibilities which are worth considering.

In the first place the coal might be burnt in boilers at a few large generating stations, and the steam raised used for driving turbines, which in turn would work dynamos for the production of electricity. By powdering the coal so finely that it can run through a pipe like a liquid, it can be made to burn at suitable jets very efficiently and almost without smoke ; the resulting electricity could be sent along wires for considerable distances to provide a naturally clean fuel. As a source of light and power electricity will, no doubt, be developed considerably in the near future, because its use is so simple, clean and by no means too expensive ; by concentrating large power stations near the coal-fields, and utilizing our water-power resources as much as possible, it will be possible to decrease the cost even more. For heating purposes, however, electricity is by no means economical ; it has been calculated that even the most efficient generating station at the present time could not make available more than one-fifth of the heating power of coal in an electrical form, but new discoveries in the future may alter this state of affairs. When considering the use of electricity for domestic heating two points must be remembered. In the first place, the ordinary open grate serves a very useful purpose in ventilating a room, whilst an electrical fire would not do this to any appreciable extent. Secondly, the cheerful coal fire with its dancing flames has become symbolic of home life to the majority of ordinary English men and women, and millions of people find solace and comfort in its warm glow on cold winter nights. There is no doubt that a time will come when the wasteful open grate will be prohibited by law, but



in the meantime it is neither necessary, nor is it desirable, to go to the extremity of electric fires.

Another method of utilizing coal economically, and in a clean manner, is to obtain gas from it for heating and lighting. Towards the middle of the eighteenth century it began to be generally known that when coal was heated in a closed vessel, out of contact with air, a gas was liberated which could be used for lighting purposes, but until the beginning of the last century these 'gas-lamps' were regarded merely as curiosities. All the important early advances in connexion with gas-lighting were made in England and in 1810 a powerful English company was formed with the object of building coal-gas works in various parts of Europe. In 1812 certain parts of London were actually lit by gas-lamps, and in 1815 the same method of illumination was introduced into Paris; in the course of time the use of gas spread, and by 1870 nearly all the large towns in Europe and the United States were illuminated by gas-lamps. The use of gas in houses for heating and lighting purposes was a further development during the latter part of the nineteenth century.

In the manufacture of coal-gas the bituminous coal is heated in fireclay retorts each holding about half a ton; these retorts were originally placed horizontally, but now there is a growing tendency to use vertical retorts which can be worked continuously. The heating is done by means of producer gas (p. 75) made by passing a limited supply of air over white-hot coke; in general a temperature of about  $1,000^{\circ}\text{C}$ . is maintained in the interior of the mass of coal in the retorts. In the absence of air the coal does not burn, but it decomposes and gives off a large amount of gaseous material which is made to bubble through water in a 'hydraulic main'; when almost all the volatile matter is driven off the residue in the retort is known as 'coke' and is almost pure carbon. Coke is a smokeless fuel, but it is difficult to ignite and produces no flame; hence in this country it is not popular for domestic grates. It gives out quite a considerable amount of heat on burning and so it is used for hot-water boilers in the home, and to some extent for steam raising. Coke is also required for the preparation of producer-gas and water-gas, and as the latter is being increasingly used as a source of hydrogen, and in connexion with possible new liquid fuels (p. 198), the demand for coke will probably increase. The

chief use of coke is for metallurgical purposes—mainly for the extraction of iron from its ores in the blast furnace. For this purpose, however, ordinary gas-coke is not suitable as it is too spongy. Metallurgical coke must be compact and hard, and in its manufacture only special ‘coking’ coals are used; actually nearly 20 million tons of this coal are carbonized in this country and over 50 million tons in the United States every year, and each ton yields about 14 cwt. of coke. At one time the coal was heated in such a way that the by-products were wasted, but in the new ‘recovery’ coke-ovens the gases, etc., are saved just as they are in the carbonization of coal for making gas.

In passing through the ‘hydraulic main’ the coal-gas leaves a certain amount of tarry matter, and of ammonia

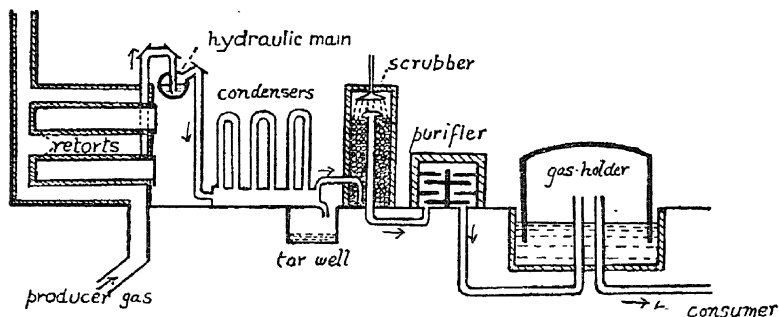


FIG. 19.—Diagrammatic Representation of a Coal-gas Works

compounds, in the water and then passes on to be purified further. In the condensers, which consist of a series of long pipes cooled externally by water, more tar separates and also more ammoniacal liquor is produced. The rest of the ammonia and some other impurities in the gas are removed by passing it through scrubbers in which water trickles over coke, and so presents a large absorbing surface. The final stage in purification is the removal of sulphur compounds which would otherwise produce a choking and acid vapour when the coal-gas was burnt. These compounds, as well as poisonous cyanides, are removed by passing the gas over trays covered with a special form of oxide of iron generally mixed with a little slaked lime; pure coal-gas passes on to the gas-holder, and the substance left behind is worked up so as to recover the sulphur and the cyanides. In Great

Britain about 17 million tons of coal are carbonized each year for the production of coal-gas, and on the average 1 ton of coal yields about 12,000 cubic feet of gas. The composition of the gas varies with the nature of the coal and with the method of heating, but a typical coal-gas may contain 46 per cent. of hydrogen, 34 per cent. of methane, 8 per cent. of carbon monoxide, 5 per cent. of olefines and benzene hydrocarbons, and the rest consists of nitrogen, carbon dioxide and oxygen impurities. There is a tendency at the present day to mix a little water-gas (p. 58) with the coal-gas—for example, by passing steam through the hot coke in the retort when carbonization is complete in order to cool it—and so a somewhat larger proportion of carbon monoxide is often present. The hydrogen, methane and carbon monoxide are the heat-producing constituents, whilst the olefines and benzene are the illuminants.

When coal-gas was first used its essential property was illuminating power, and special methods were frequently adopted in order to increase this by introducing various oils; at the present time, however, heating power is the essential quality of a gas. For lighting purposes the old gas jet is now obsolete and the value of the gas mantle, which is so widely used as a source of illumination, depends on the production of a high temperature. The heating efficiency, or calorific power, of a gas is expressed in British Thermal Units (B.Th.U.) per cubic foot; one unit is the amount of heat required to raise the temperature of 1 pound of water through 1° Fahrenheit. An average coal-gas has a calorific value of roughly 500 to 560 B.Th.U. per cubic foot. Since the quality of gas is now judged by its heating power, it is obviously rational to pay for the gas according to its calorific value; this is generally being done in this country at the present time in the system of payment by the number of 'therms' used. One 'therm' is 100,000 B.Th.U., and hence we are paying not for the quantity of gas consumed, but for the amount of heat which is supplied.

The tarry and ammoniacal liquors obtained from the hydraulic main and in the condensers and scrubbers used in the first stages of gas purification (p. 191) were at one time thrown away, but they are now worked up and provide a number of useful substances. The watery ammoniacal liquor is separated off and heated by passing steam into it; most

of the ammonia is liberated in this way but the remainder can be set free by the addition of lime. The vapour is passed into sulphuric acid, and ammonium sulphate crystals separate out after a time ; this substance, under the name of ' sulphate of ammonia ', is almost entirely used as an artificial fertilizer. Every ton of coal can yield, on the average, 7 pounds of ammonia, which produce 26 pounds of ammonium sulphate, and since nearly 40 million tons of coal are carbonized in Great Britain every year, either for gas or coke manufacture, the annual output of sulphate of ammonia from coal is about 400,000 tons. This amount is being supplemented, at the present time, by synthetic ammonia made from atmospheric nitrogen, and in this connexion new processes are being developed for obviating the use of expensive sulphuric acid. Small quantities of ammoniacal liquor and ammonium salts are used for other purposes, besides fertilizers—in refrigerating machines, and in explosives, for example—but by far the larger proportion of the ammonium salts made is used on the land.

The tar obtained during the carbonization of coal was at one time thrown away, but gradually various minor uses were found for it ; at first it was boiled in open pans and the residual pitch used for roofing materials, and later the vapours coming off were condensed and used as a turpentine substitute. Various distillation products were obtained from coal-tar but there was no great demand for these ; the discovery of the aniline dyes by Perkin in 1856 (p. 219), however, stimulated the production of artificial colouring matters, and later of many other substances, the raw materials for which are obtained from tar. On the average 1 ton of coal yields about 1 cwt. of tar and at the present time more than one and a half million tons of tar, resulting from the carbonization of nearly 40 million tons of coal, are distilled in Great Britain each year ; in the United States over 2 million tons of tar are worked up whilst in the whole world it is estimated that about 6 million tons of tar are treated per annum.

Tar contains at least 200 different substances, but the majority of these are found in extremely small amounts ; only a few of the constituents are present in quantities worth extracting. The distillation of tar is carried out very much in the same way as the refining of crude paraffin ; the tar is placed in air-tight retorts, or stills, and gradually heated.

The vapours coming off between various ranges of temperature are condensed and collected in separate fractions. The compositions of these fractions depend on the nature of the coal from which the tar was obtained, on the method of carbonization used, and also on the range of temperature between which the liquids distil; these fractions vary from place to place but in general four fractions are obtained from coal tar.

The first liquid to distil over is called the 'light oil'; this consists mainly of a mixture of benzene, toluene and xylenes separable by further distillation. On purification these form the raw materials for the preparation of the so-called 'aniline dyes' and many other useful materials. Toluene is used in the manufacture of the explosive T.N.T. (p. 114) and for the sweetening agent, saccharin (p. 238). A mixture of benzene and toluene, known as 'benzole', is used as a motor spirit and has excellent anti-knock properties; a good deal of this motor-benzole is recovered from coal-tar by cooling after passing through the condensers. One ton of coal will generally yield about a gallon to a gallon and a half of motor spirit, or, if separated into its constituents, roughly 12 pounds of benzene and 3 pounds of toluene. The higher boiling point fraction of the light oil is known as 'solvent naphtha'; it is used as a solvent in the rubber industry, especially in the manufacture of water-proof materials.

The second fraction obtained from coal-tar is called the 'middle, or carbolic, oil'; this consists chiefly of carbolic acid, or phenol, and naphthalene. These substances are separated from one another and the products, generally consisting of  $\frac{1}{2}$  pound of phenol and  $\frac{3}{8}$  pound of naphthalene per ton of coal, are widely used in the synthetic dye industry. Carbolic acid is a powerful disinfectant and finds application in surgical work; one of the most important of its products is picric acid, which is a yellow dye as well as the chief constituent of the explosive known as 'lyddite' (p. 114). Impure forms of carbolic acid are finding considerable application now-a-days in the manufacture of artificial resins of which 'bakelite' is probably the best known. Pure naphthalene is frequently sold as 'moth balls' to protect furs and fabrics from attack by insect pests, whilst an impure form mixed with saw-dust is made up into fire-lighters. Naphthalene is one of the most important of the raw materials required for the production of synthetic indigo (p. 162).

The next coal-tar distillate is the 'heavy, or creosote oil'; this consists of a mixture of a number of substances which are rarely separated. The oil as it distils is used for the preservation, or 'creosoting' of timber; a creosote paint is also often used for this purpose. The final fraction is known as 'anthracene oil' and its chief constituent is the hydrocarbon anthracene used in the production of dyes, particularly alizarin (p. 219). The residue left in the still is 'pitch', to the extent generally of about 75 to 80 pounds per ton of coal; this is used for road work and also for making 'briquettes' from coal dust. The direct coal-tar products benzene, toluene, xylene, phenol, naphthalene and anthracene, are the parent substances for the manufacture of about 300 secondary products, or 'intermediates', and from these about 1,500 finished materials are made; more than three-quarters of these are dyestuffs and the rest are used as perfumes, flavouring essences, medicines, antiseptics, explosives, etc. These substances are often referred to in a general way as 'coal-tar products'; it must be clearly realized, however, that they are not actually present in coal-tar, but are only obtained as a result of a complicated chemical treatment of the distillation products.

By the carbonization of coal, therefore, it is not only possible to obtain two smokeless fuels—coke and gas—but in addition many valuable substances, forming the raw materials for important chemical industries, are recovered from the tar which would otherwise be wasted in the form of smoke and soot. If all the consumers of coal for heating purposes could be persuaded to use coke or gas, instead of burning coal directly, it would be possible to obtain in this country at least 150 million gallons of benzole each year for use in motor-car engines, whilst many other substances would be available for chemical manufactures. Unfortunately new and expensive plant would be required for the consumption of gas fuel, and in any case coal is cheaper to use at present; for a given sum of money it is possible to obtain twice as much heating power from coal as from gas. In some towns, however, large industrial consumers are being supplied with gas at a specially cheap rate; this fact, coupled with the great convenience and cleanliness in use, will probably mean an increased use of gaseous fuel with all its consequent benefits. Gas fires for domestic purposes are increasing in

number, and the newer types are said to be just as efficient for ventilation purposes as a coal fire; the cost of the gas fire is not yet low enough and the appearance not cheerful enough, however, for the coal fire to be entirely displaced.

In the third method for treating coal we may have a solution of various fuel and smoke problems. Instead of carbonizing coal at a temperature of about  $1,000^{\circ}\text{C.}$ , a much lower temperature is used, generally in the vicinity of  $600^{\circ}$  to  $700^{\circ}\text{C.}$ ; this is called the 'low temperature carbonization' process, and it yields products very different from those obtained in ordinary carbonization. The residue in the retorts is something between coke and coal; it only contains 4 or 5 per cent. of volatile matter and is said to burn readily in an open grate producing flame but no smoke. One ton of coal leaves from 12 to 14 cwt. of this semi-coal in the retort. Such a fuel is already on the market under the name of 'Coalite'. A much smaller quantity of gas is obtained than in the high temperature method of carbonization—5,000 to 6,000 cubic feet per ton of coal—but its calorific power is as high as 700 to 800 B.Th.U. per cubic ft. A large quantity of tar is obtained—about twice the amount produced in the ordinary way—but its nature is quite different from that which results from high temperature carbonization. The composition of the tar varies very considerably with the actual temperature and method used in the treatment of the coal; in general it is found that benzene, toluene, xylene, naphthalene and anthracene are absent, but instead there are a number of paraffin hydrocarbons which can be used for motor fuel. It has been found that on distillation the tar from 1 ton of coal will yield, on the average, from 2 to 3 gallons of refined motor spirit, and in addition there can be obtained 9 gallons of oil suitable for use in Diesel engines; low temperature tar also contains a large proportion of carboic acids which may be used in the manufacture of explosives, for synthetic resins and for preserving timber. A great deal of experimental work has been performed with the object of overcoming the engineering difficulties that are encountered in the low temperature carbonization process, and considerable progress has been made. Already a number of plants are operating successfully in this country and an increase may be expected in the future; the so-called 'L and N' process is particularly interesting, as it makes use of coal slack of which a large

proportion would otherwise be wasted. It is fairly certain that the low temperature process will not entirely replace the old high temperature method of coal carbonization, because the former produces less gas, and the tar does not yield the important parent substances required for dye manufacture; but as a help in solving the smoke problem and as a means of providing a liquid fuel for internal combustion engines the low temperature carbonization process is likely to have a future.

It has already been mentioned that the known petroleum resources of the world will be used up in a comparatively few years (p. 185) if the present rate of consumption is continued; the great increase in motor transport and the tremendous progress being made in aviation will mean, probably, an increase in the amount of liquid fuel used. The internal combustion motor is such a convenient power unit that, unless some startling new discovery is made in the future, the demand for petrol, or petrol substitutes, will continue for very many years, and so it is necessary to look around and see if liquid fuels may be obtained on a large scale from sources other than petroleum.

The first possible motor fuel to consider is alcohol; this can be made by the fermentation of starchy and sugary substances (p. 158). The raw materials must be cheap and the following have been suggested: figs, prickly pear, palm sap, potatoes, beets, artichokes, mangolds, maize and molasses. Already a number of factories are producing alcohol on a large scale from molasses, but at the present time the price is too high for it to compete with petrol as a fuel; if the cost of the latter should increase, however, then power alcohol production might be an economic possibility. Waste wood, and other cellulose materials, can be hydrolyzed by acid solutions to form glucose and other simple sugars; these may then be fermented, by means of the appropriate enzymes, to yield alcohol. At present the hydrolysis process is costly and so a search is being made for a micro-organism which can be cultivated and is capable of carrying out the hydrolysis of cellulose under suitable conditions.

There are certain disadvantages in the use of alcohol; the engine is not so easy to start when cold as with petrol and the mileage to the gallon is less; on the other hand a greater engine compression may be used and so more power



obtained (p. 115). A mixture of alcohol, petrol and benzole, known as Discol, has been placed on the market as a motor fuel; the hill-climbing capacity and smooth running of the engine are said to be increased, whilst 'knocking' is absent. Important discoveries, however, will have to be made before alcohol motor spirit comes into general use.

Some authorities consider that the most probable rival to petrol, in the near future, will be methyl alcohol; this provides an easy-starting, anti-knock fuel but the mileage per gallon is less than with petrol. The new synthetic process for the manufacture of methyl alcohol from water-gas has already been described (p. 178). When the cost of production is further decreased, as it probably will be shortly, as a result of improved technique and better catalysts, petrol will find a very serious competitor. The raw materials for methyl alcohol production are coke and water, and the supplies of these substances are not likely to be exhausted for many years.

By means of some slight modifications of the process for making methyl alcohol from a mixture of water-gas and hydrogen, a more complex liquid fuel known as 'synthol' has been obtained. The temperature is higher— $400^{\circ}$  to  $435^{\circ}$  C.—but the pressure is lower—75 to 150 atmospheres—and the catalyst is somewhat different; Fischer, in Germany, has used iron coated with alkali, such as sodium or potassium carbonate, as the catalytic material. The product contains a number of more complex alcohols, some hydrocarbons and other compounds; it is stated to be a more economical fuel, as regards mileage per gallon, than methyl alcohol. The proportion of gas converted into liquid fuel is, however, low and so in the long run methyl alcohol proves to be the cheaper product; it is possible that a mixture of methyl alcohol and synthol, combining the advantages of both, may be a valuable fuel of the future.

One more process for the production of liquid fuel is worth mentioning because it may have important consequences; this is known as the Bergius process for the 'hydrogenation' of coal. Powdered coal is mixed with about its own weight of oil, or tar, in order to form a thick paste; a little oxide of iron is added and the mixture placed in a very strong vessel and heated to nearly  $500^{\circ}$  C. At the same time hydrogen gas at a pressure of nearly 200 atmospheres is passed in until a black tarry liquid results. The latter is then

distilled and it is claimed that from one ton of coal there may be obtained 40 gallons of motor fuel with good anti-knock properties, 50 gallons of Diesel engine oil and 10,000 to 12,000 cubic feet of gas. The residual tar may be used for working up the next batch of coal for hydrogenation. The process has the great advantage of producing a large amount of motor spirit and also of being applicable to coal-dust, but there are disadvantages ; these are, firstly engineering difficulties, secondly the high cost of hydrogen, and thirdly the high cost of heating. The first difficulty is being overcome, and the other two may be met to some extent by using the gas produced during the process. Cheap hydro-electric power, for heating purposes, and for making hydrogen from water would be a great help towards the production of a cheap liquid fuel from coal. It is claimed that in Germany the Bergius process is working successfully and that motor spirit, at the rate of nearly 60 million gallons per annum, will be produced from lignite in 1929. When the supplies of petrol become exhausted the Bergius process may help to provide an economic liquid fuel, especially if some of the world's great peat and lignite deposits could be utilized.

It will be noted that all the possible processes for the production of petrol substitutes, except ethyl alcohol, involve the use of coal, or coke, and the question naturally arises as to how long our coal resources are likely to last. Of course it is impossible to calculate the amount of coal available with any exactness, but a number of interesting estimates were made by the International Geological Congress in 1913. The total amount of all kinds of coal—anthracite, bituminous coal and lignite—within the first 6,000 feet of the earth's crust was said to be over 7,000,000 million tons, or approximately 6,000 times the world's annual consumption. At the present rate of use the coal resources of the world should thus last 6,000 years. Of these resources 51·8 per cent. were considered to be in the United States, 16·4 per cent. in Canada, 13·5 per cent. in China, 5·7 per cent. in Germany and 2·6 per cent. in Great Britain. Professor H. Stanley Jevons calculated in 1915 that the coal reserves of Great Britain were about 197,000 million tons within 4,000 feet of the surface and this, after allowing for pit wastage, should last, at the present rate of consumption, about 600 years. It is quite clear that we need not fear any shortage of coal in this country

for several centuries, but a time may come when we shall be dependent on the United States, or even China, for our coal supplies. For the sake of posterity we can only hope that before this time comes other methods of utilizing energy, for example that of the atom (p. 36), may have been developed to such an extent as to make us independent of coal. In the comparatively near future, however, it is probable that coal and lignite will play a great part in industry, not only for the production of gas and smokeless fuel, but also as the chief sources of liquid fuel for the ubiquitous internal combustion engine.

#### QUESTIONS

1. How was coal probably formed ?
2. How is coal-gas made and purified ?
3. What is meant by low temperature carbonization ? What are its advantages and disadvantages ?
4. What is a 'therm' ? Why do we pay for gas by 'therms' ?

#### SUBJECTS FOR ESSAYS AND DISCUSSION

1. Coal-tar products.
2. The uses of coal.
3. Coal conservation and the smoke nuisance.
4. Liquid fuels from coal.

#### FURTHER STUDY

1. Chemistry as an aid to the coal industry.
2. The future of coal.
3. Power alcohol.
4. Coal-tar distillation and the isolation of the products.

#### BOOKS TO READ

Old Trades and New Knowledge. Bragg. (Bell.)  
Creative Chemistry. Slosson. (Univ. of London Press.)  
Achievements of Chemical Science. Philip. (Macmillan.)  
Coal and its Scientific Uses. Bonc. (Longmans, Green.)  
Coal Carbonization. Porter. (Chemical Catalog Co., U.S.A.)  
Coal Carbonization. Roberts. (Pitman.)  
Books recommended for Chapter XV.

#### SUGGESTIONS FOR EXPERIMENTS

Distillation of coal.  
Distillation of tar.  
Examination of various coal-tar products in a pure form.  
Visit to local gas works.

## CHAPTER XVII

### METALS AND ALLOYS

A VERY important factor in the progress of civilization has been the development of the use of various metals by man. Gold and copper were probably the first metals to be used, since they occur in the free state in Nature ; the rocks and other associated impurities were crushed and washed away until only the metal remained. This residue could then be beaten out into sheets or else melted to form lumps which might be hammered into various shapes. Both gold and copper are soft metals and although attempts were made to use the latter for tools and weapons it was not altogether satisfactory. At that time, that is up to 5,000 years ago, it could not have been realized that minerals contained various metals locked up in the form of chemical compounds ; the appearance of the rocks and stones would certainly not have suggested that they contained any metal. It was, however, probably by accident the discovery was made that useful metals might be obtained from some rocks ; a circle of stones may have been used for holding a wood fire and after the fire had burnt out, a lump of metal may have been discovered amongst the ashes. The rock was a metal ore, probably an oxide, and the carbon produced from the wood in the fire had combined with the oxygen of the ore and left the metal behind. In this manner, probably, both copper and tin were first smelted and later people learnt by experience to discriminate between ores which could be made to yield one metal or another when 'burnt' in a wood fire.

It has already been mentioned that the first copper tools were very soft, but at some time it was discovered that by the addition of tin to the copper a much harder metal—what we now call an alloy of tin and copper—was produced. Thus some unknown experimenter discovered bronze, and during the Bronze Age, founded in this way about 3000 B.C., not

only were tools, weapons and utensils made from this alloy but it was also used for decorative and artistic work. In the course of time the ancient peoples learnt how to obtain and work other metals ; in the Old Testament we find mentioned gold, silver, copper, iron, lead and tin, and although we cannot be certain that the translations are correct, yet we know that all these metals were used before the commencement of the present era. The development of chemical knowledge in the last 2,000 years has resulted in a better understanding of the methods of extracting metals from their ores ; not only do we know how to obtain them easily from minerals but we have a greater variety of metals at our disposal, and so at the present time many metals and alloys fulfil an important function in everyday life.

We now know that most metals are found in the earth not in the free state but in minerals consisting generally of carbonates, or of compounds of the metal with oxygen or sulphur, that is as oxides or sulphides. In order to obtain the metal the ore is first crushed and the earthy matter removed, often by washing ; sulphide and carbonate ores are then roasted to convert them to oxides. The product is mixed with carbon, or some other element which can combine readily with oxygen, and heated ; the metal in a more or less pure condition is then left behind. The actual details of the process vary very considerably with the nature of the metal and often a quite different method than that described has to be adopted. The most important metal of modern times is iron, and in fact we are still to-day in the Iron Age which replaced the Bronze Age thousands of years ago. At present the world is using about 70 million tons of iron every year for various purposes ; this amount is greater than the total of all the other metals used. Not only is iron cheap and easy to obtain, but it possesses certain remarkable properties which make it an exceptionally useful metal ; by adding small quantities of other elements and by differences of treatment it is possible to obtain alloys which are hard or soft, brittle or able to be hammered, magnetic or non-magnetic, elastic or non-elastic. In fact iron is a veritable Proteus amongst metals and hence very many different uses for it have been found.

The chief ores of iron consist of the oxide or the carbonate : and the metal is ' smelted ' in a ' blast ' furnace which is

generally 80 to 100 feet in height and about 25 feet across at its widest part. These furnaces work continuously and yield about 1,000 tons of cast iron per week. In the smelting process the ore is mixed with metallurgical coke and some limestone and fed in at the top of the furnace whilst a blast of hot air is blown in from the bottom. The oxygen of the air and the carbon of the coke unite to form carbon monoxide and at the same time sufficient heat is liberated to keep the whole mass in the furnace at a very high temperature. The carbon monoxide gas reduces the iron ore down to metallic iron, and the latter, generally containing about 3 to 4 per cent. of carbon and small quantities of silicon, sulphur, manganese and phosphorus, melts and collects as a liquid at the bottom of the furnace; from time to time the molten metal is run off into moulds and on cooling forms 'pigs' of cast iron. Since nearly all iron ores contain clay and other impurities a method has to be adopted for their removal, and it is for this purpose that the limestone is added with the iron ore and coke in the blast furnace. On heating, the limestone produces lime and this combines with the clay and many other impurities to form a liquid 'slag' which collects on the surface of the metal. This slag is run off, cooled and generally thrown away; in recent years, however, some slags have been used for cement-making and for road material.

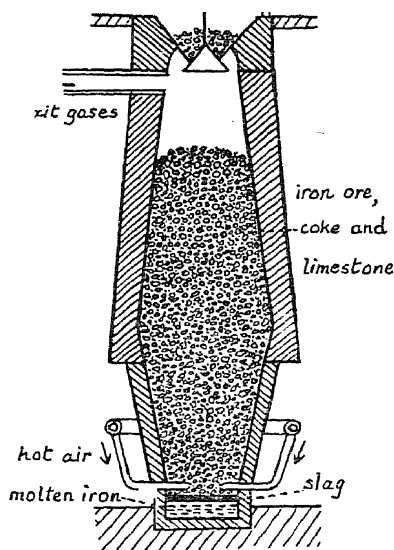


FIG. 20.—Blast Furnace for the Production of Iron from its Ores

Pig iron is very brittle owing to the presence of a large proportion of carbon, and so it cannot be hammered, but as it melts easily it is used for making castings. In order to be workable iron must be fairly pure, and 'wrought iron' which can be hammered into various shapes contains only

about 0.2 per cent. of carbon. This form of iron is obtained by oxidizing the excess of carbon present in pig iron by means of an oxide of iron under suitable conditions; a very pure malleable form of iron results. Wrought iron is used for welding, for making rivets and in all branches of a blacksmith's work; its softness, unlike that of steel (p. 205), is not affected by heating and sudden quenching.

Steel contains a little more carbon than wrought iron but less than cast iron; in addition there are usually present small amounts of other metals such as manganese, chromium, vanadium, nickel, tungsten or molybdenum which are included in order to confer special properties on the steel. Sulphur and phosphorus must be almost completely absent otherwise

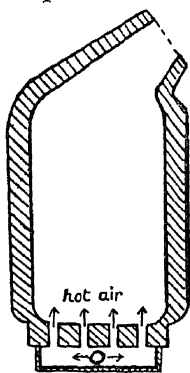


FIG. 21A

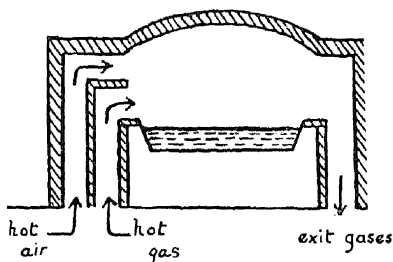


FIG. 21B

#### Steel Furnaces

Bessemer converter (left) and Siemens' open-hearth furnace (right)

the metal will be brittle. A common way of making steel is by a method invented by the Englishman, Henry Bessemer, in 1855; this discovery marked one of the greatest advances in the metallurgy of iron because by the new process large quantities of steel could be produced quickly and cheaply. About ten tons of molten iron from the blast furnace are run straight into a large pear-shaped iron vessel called a 'converter' and a stream of hot air is blown through the liquid until the impurities are converted into oxides. The carbon is burnt up and the silicon is turned into an oxide which passes into the slag; when these and other impurities are removed a definite quantity of cast iron containing carbon and manganese is added to the converter in order to produce

steel of the desired composition. In the early days the converter was always lined with silica bricks but this was no help in removing the undesirable phosphorus, and so in 1879 Gilchrist and Thomas suggested using a lining of lime and magnesia when working with ores rich in phosphorus; this takes up the oxidized phosphorus and forms a slag containing phosphates which is solidified, powdered and sold as a manure under the name of 'basic slag' (p. 170).

Owing to the difficulty of controlling the Bessemer process it is being replaced to a great extent by the 'open-hearth' method which was first used in 1856. Molten cast iron is run on to the hearth of a large flat furnace and enough oxide of iron is added to oxidize impurities; when this process is complete the requisite amounts of carbon, manganese and other elements are added. The furnace is lined with silica, or with lime and magnesia, according as the ore is poor or rich in phosphorus, as in the Bessemer process. The open-hearth method is slower than the other but the products are more uniform. For the manufacture of special steels which may not be required in large amounts smaller furnaces called 'crucibles', generally heated electrically, are used; when the impurities are removed exact amounts of various substances are added in order to produce perfectly definite alloys.

If we consider carbon steels first we find that the hardness increases as the carbon content increases; mild steel contains up to 0.2 per cent. of carbon, structural steel 0.2 to 0.6 per cent., whilst tool steel may have 0.9 to 1.5 per cent. of carbon. The first two types of steel can be worked and welded almost like wrought iron. One of the curious facts about steel is the variation in properties resulting from 'heat treatment'; when the metal is heated to redness and suddenly cooled by plunging into water it becomes very hard but extremely brittle. If this steel is slowly heated to certain temperatures and allowed to cool gently it develops properties depending on the temperature to which it is heated; this is the operation known as 'tempering'. The operator can generally judge the temperature by the colour of a thin layer of oxide which forms on the steel; the higher the temperature the darker is the colour and the softer is the resulting metal. A pale yellow coloured film, corresponding to a temperature of 220° C. to 230° C., is used for tempering steel for very sharp tools, such as razor blades; a purple colour and a temperature



of about  $280^{\circ}\text{C}$ . are used for cutlery, whilst a temperature of about  $300^{\circ}\text{C}$ ., indicated by a dark blue film, is suitable for tempering steels for chisels and saws.

The great variations in the properties of iron which result from heat treatment and from changes in the carbon content are due to two factors ; in the first place iron itself can exist in three different crystalline forms, or allotropic modifications (p. 71). Each of these forms is stable over a certain range of temperatures and each has its own specific physical—including magnetic—properties. The other factor is that carbon can exist in iron in several different conditions ; it may exist in the free state in the form of graphite, it may be dissolved in the solid iron, or else it may be present as a compound of iron and carbon known as 'cementite'. The particular form in which the carbon is present and the modification in which the iron exists depend on the proportion of carbon in the steel, on the temperature to which the alloy has been raised and on the rate of cooling ; all these factors, therefore, will influence the properties of the iron-carbon alloy called by the general name of steel. Small amounts of certain metals, such as manganese and nickel, often retard the change of one form of iron to another and so for this and other reasons they affect the physical properties.

Although iron is a very valuable metal, it has one great drawback ; that is, its tendency to corrode away or rust. All the common forms of iron become covered with a layer of reddish rust when exposed to moist air ; this corrosion of the iron is most rapid in manufacturing districts where the atmosphere contains acid vapours produced in the burning of coal and in other ways. Sir Robert Hadfield has estimated that the wastage of iron which the world suffers every year due to corrosion costs something like £500,000,000 to replace ; the problem of preventing the rusting of iron is thus one of prime importance. Although a great deal of work has been done on the corrosion of iron we are not yet certain as to its exact mechanism ; we do know, however, that it is due in some way to the presence of moisture and oxygen which attack the iron and produce some form of oxide. This oxide constitutes the rust which is porous and breaks away from the surface, thus leaving fresh metal exposed to undergo further corrosion.

The simplest way to avoid corrosion is clearly to prevent

the air from having access to the iron by coating it with a thin layer of some more resistant metal. One way of doing this is to dip a sheet of clean iron into a bath of molten tin ; thus a film of tin, which does not rust in air, is made to cover the whole of the iron. In this manner we obtain the 'tin-plate' used for making 'tin' containers of various kinds, and for cheap domestic utensils ; it is produced to a great extent in South Wales. Tin-plate, however, has a great disadvantage ; if the tin is scratched so that the iron is exposed, then rusting will take place even more rapidly than if the tin were not present. Galvanized iron is another form of protected iron ; here the sheet of metal is coated with a thin layer of zinc. The zinc forms an adherent coating of zinc oxide which prevents further corrosion of this metal or of the iron which it covers. Galvanized iron is not used for utensils or for containers because the zinc would be readily dissolved away by the acids present in various food materials. Nickel plating of iron is frequently used to protect the latter metal from corrosion ; as a rule a layer of nickel about a thousandth part of an inch in thickness is applied by electrolysis of a solution containing a salt of nickel. The electro-plating of nickel, as the process is called, is not by any means a simple matter because the deposit often tends to become pitted with small holes or to peel off in thin layers ; both these conditions will cause increased corrosion of the iron which the nickel is meant to protect. Within the last year or two chromium and cadmium plating have been developed for the protection of iron from rusting. It is worth mentioning that wrought iron rarely rusts because when it is heated in order to be hammered it becomes covered with a thin layer of adherent oxide, called 'mill-scale', which prevents further access of air ; wrought iron has thus generally a dark colour due to this oxide film.

In recent years there has been a new development towards the production of rustless and non-corroding forms of iron and steel. In 1913 Brearley, of Sheffield, when searching for a material suitable for gun-linings, made the chance discovery that an alloy of iron and the metal chromium, when suitably heat-treated, was remarkably resistant to corrosion. This led to the production of 'stainless steel' for cutlery purposes ; it was first introduced in 1914 and has become increasingly popular ever since. Most of these steels contain 12 to 15

per cent. of chromium and 0.25 to 0.40 per cent. of carbon ; the chromium imparts the non-corroding property whilst the carbon allows the steel to be tempered. In this way a great variety of stainless steels may be obtained for various purposes and they can be given, in spite of reports to the contrary, just as sharp an edge as ordinary steel. By adding nickel to chromium steel it is possible to obtain an alloy which is even more resistant to corrosion ; an alloy containing about 18 per cent. of chromium and 8 per cent. of nickel appears on the market as ' staybrite '. This metal is very tough, yet it can be pressed or hammered into almost any form ; it cannot be hardened by heating and quenching and so is of no use for tools or cutting instruments. Staybrite steel is being used in increasing amounts in chemical works where corrosion resistance is important.

It has already been mentioned that various metals are able to influence the properties of steels and some of these effects will now be discussed. Let us consider in the first place the result of adding manganese to steel. As long ago as 1773 it was known that manganese destroyed the magnetic properties of iron, which is, of course, the most magnetic of metals. Manganese steel is almost non-magnetic, and hence it is used for the bulkheads of warships, for the wheel-houses of trawlers and for other parts of ships' structures which are close to the magnetic compass used for steering purposes. The most important and remarkable property of manganese steel, however, is that when it is heated and suddenly quenched, instead of becoming brittle and hard, it becomes very tough and remarkably strong. The alloy is so tough that it cannot be planed or drilled in the ordinary way ; it is generally used in the form of castings, or else it is worked hot and rolled or hammered. The latter treatments have the effect of making the steel still tougher. An average manganese steel may contain 12 per cent. of manganese, 1 per cent. of carbon and 0.5 per cent. of silicon ; it is used wherever there is likely to be hard wear, as for example for tram and train rail crossings, junctions and sharp bends ; burglar-proof safes and crushing machinery are also made from the same material. Manganese steel was used during the war for making steel helmets ; the impact of a bullet or piece of shrapnel might cause a dent but could only penetrate the metal with great difficulty.

Another important metal which is frequently used to alloy with iron is the element nickel. Steels containing about 3 to 5 per cent. of nickel have a high elasticity and great strength ; they are used for armour plates, steel-framed buildings and motor-car parts. As the proportion of nickel increases the elasticity decreases but the hardness increases and steels containing 15 per cent. and more of this metal will stand great strains without breaking ; such alloys are used for machine parts which are liable to be struck hard blows. When the proportion of nickel is increased to about 25 per cent. an alloy is obtained having a high electrical resistance which varies little with temperature ; it is, therefore, used for making standard electrical resistances. This alloy is, incidentally, non-magnetic. One of the most remarkable nickel-iron alloys is known as 'Invar' ; it contains 36 per cent. of nickel, 0.5 per cent. carbon, 0.5 per cent. manganese and the rest iron. On heating, unlike almost all other metals and alloys, it does not expand to any appreciable extent, neither does its elasticity alter with changes in temperature. Invar is also non-corrodible and can be rolled, forged or drawn into threads. It is invaluable for springs of accurate chronometers which must not alter their length or elasticity with variations in temperature. The alloy is also used for measuring instruments of various kinds, for pendulum rods and for dividing engines ; in each case invariability of length is most desirable. Two other alloys of nickel and iron are particularly interesting ; the first of these is called 'platinite' and contains 45 per cent. of nickel and a very little carbon. On heating or cooling it expands or contracts to the same extent as glass and so it was used for sealing the metal filaments into electric-light bulbs and wireless valves. If the contraction of the metal used for sealing were greater than that of glass, then on cooling the seal would not be air-tight ; if, on the other hand, it were less, then the glass would crack. At one time the costly metal platinum was used for sealing through glass and this was first replaced by the cheaper 'platinite' ; at present an alloy similar to 'invar', coated with a thin film of copper, is generally used. The last nickel alloy to be mentioned is known as 'permalloy' containing only one-fifth of iron ; it is very easily magnetized, but it also loses its magnetism very readily when the magnetizing force is removed. It is specially useful for submarine

telegraph cables, for when the core of the latter is surrounded by a layer of 'permalloy' the speed of sending signals can be increased to about five times the ordinary rate.

Tungsten is often used to alloy with iron, together with a little chromium or manganese, because the resulting steels retain their hardness at high temperatures. When used in a lathe working at high speed a cutting tool is liable to become red hot and an ordinary steel tool would lose its edge under these conditions; a tungsten steel tool, however, remains sharp at 700° C. This material is often known as 'high speed' steel; it is also used for drills and for boring machines. A good steel of this kind may contain about 14 per cent. of tungsten, 4 per cent. of chromium, 1 per cent. of vanadium and 0.5 per cent. of carbon. Tungsten may be replaced quite satisfactorily by the more expensive metal molybdenum, since a smaller amount of the latter is required than of the former. Such steels are used for armour-piercing shells, aeroplane struts, automobile axles and propeller shafts.

In recent years a large number of new steels of various types have been devised in order to answer different purposes, and these may contain not only one but several of the metals which have just been discussed individually. The tendency at present is to prepare these special steels in small amounts at a time, using electric furnaces heated by induction; by this means the exact composition, and consequently the properties, of the resulting steel may be very carefully controlled.

Next in importance to iron comes the metal copper. In the pure state it conducts the electric current extremely well and so it is used for electric wires and cables. A trace of impurity, however, is often sufficient to ruin this conducting power. Copper is also a good conductor of heat, and so it is often used for kitchen utensils, and in the works for large evaporating pans, etc., which have to be heated externally. The softness of copper was known to the ancients who found that the addition of about 10 per cent. of tin would increase the strength and hardness. This alloy is known as bronze and its properties vary with its composition. Pure copper cannot be cast at all easily, because the molten metal dissolves various gases which are set free on cooling and so produce blisters and blow-holes; the addition of tin, however, prevents the gases from dissolving and so bronze gives good castings.

For this reason an alloy containing 4 per cent. of tin, 1 per cent. of zinc and the rest copper is used for the bronze, or the so-called 'copper', coinage. Soft-bronze, or 'gun-metal', is a stronger alloy and contains from 8 to 12 per cent. of tin ; it is used for making various scientific instruments. Hard bronze, or 'bell-metal' contains up to 24 per cent. of tin ; it is quite hard and so when made into a bell it can withstand the blows of the clapper. If the tin content is increased to 33 per cent. a white metal is obtained which can take a high polish and does not tarnish ; it is used for making mirrors and is called 'speculum metal', or 'mirror metal'. It is interesting to note that this metal was actually used for mirrors by the Romans and was made at Brindisi (Brundisium), from which the name 'bronze' is said to be derived. By adding a few per cent. of phosphorus to bronze the resulting alloy—'phosphor bronze'—has an increased hardness and is less corrodible by sea water than is iron or steel ; it is, therefore, used for machine parts, bearings, pump parts, etc., which are liable to come into contact with sea water. The alloy will withstand considerable friction without wearing away.

Another notable group of copper alloys are the brasses, which contain zinc in varying proportions ; with increasing zinc content the alloys become lighter in colour and their strength and hardness also increase. The common alloys contain from 20 to 40 per cent. of zinc ; they have a golden yellow colour, can be readily polished and are not easily tarnished. Brass is chiefly used for castings, for machine parts and for cartridge cases. An alloy containing 40 per cent. of zinc is called Muntz metal ; it can be machined when hot and is very resistant to corrosion and so it has been used as a sheathing for ships. An important alloy of copper and nickel containing up to 60 per cent. of the latter element, known as 'monel metal' has come into prominence in recent years. It is more resistant to corrosion than bronze or brass, and it can be readily cast, rolled or drawn into wire. Monel metal is being increasingly used for marine work, particularly for condenser tubes, and for laundry, dairy and restaurant equipment.

Two other valuable metals are lead and tin ; these have been known for a considerable time, but for long they were not distinguished from one another. They both melt very

easily but lead is a much heavier metal than tin ; the former also oxidizes and tarnishes in air more readily than does the latter. Lead is used for water pipes, for roofing purposes and in the manufacture of accumulators. It is also used for making 'white-lead', which is a basis for many paint materials ; unfortunately the poisonous nature of lead is making this efficient product unpopular. Tin is used for making tin-plate, to which reference has already been made ; it is also beaten out into thin sheets known as 'tin-foil' or 'silver-paper', used for wrapping chocolates, tobacco, etc. Solder and pewter are alloys of lead and tin in varying proportions, whilst type-metal and other easily molten alloys contain either tin or lead, or both, with other metals.

One of the most remarkable developments of recent years concerning metals has been in connexion with aluminium. It was first made by Wöhler in 1827, but until about forty years ago it was regarded merely as of chemical interest and as having no practical applications, chiefly because it was so difficult to extract from its ores. Between 1886 and 1890, however, two similar but independent processes were developed, by Hall in America and by Héroult in France, by means of which it was possible to make aluminium metal on a large scale ; although the principle of the process used to-day is the same as the original one, improvements of technique have resulted in a greatly decreased cost of the metal. In 1886 aluminium cost about thirty shillings a pound ; at the present time the price is little over a shilling, and the annual world production is about 170,000 tons. The raw material for the extraction of aluminium is a mineral called 'bauxite' which is found chiefly in the South of France, in Arkansas, U.S.A., and in British Guiana. The mineral consists mainly of an oxide of aluminium which must be purified before it can be used further. The pure oxide is dissolved in molten cryolite—a mineral found in Greenland—and an electric current is passed through the solution ; metallic aluminium separates at the negative electrode in a molten condition and is run off from time to time. The process can only be worked economically where electricity, obtained from water power, is cheap ; in this country the British Aluminium Corporation are extracting the metal at Dolgarrog in N. Wales and at Kinlochleven in Scotland.

The important points about aluminium are that it is a

light metal, its density being 2·7 as compared with 7·9 for iron, it is quite strong and is an excellent conductor of heat and electricity. It is superficially oxidized in air but the film of oxide adheres so firmly to the metal that further corrosion is prevented. Aluminium, owing to its good heat conductivity, is widely used for kitchen utensils; since the metal is attacked by alkalis it is not advisable to use soda when cooking in or cleaning these vessels. Aluminium is replacing copper for electric power wires, especially in America, as it is so much lighter and cheaper, although not quite such a good conductor. The metal in powdered form is used for making the silver-like aluminium paint and also in the Thermit process (p. 95) for welding rails, etc.

Owing to their extreme lightness and strength alloys of aluminium are finding increasing uses in the construction of aircraft, and for motor-car parts. The alloy 'magnalium' is particularly interesting; it consists mainly of aluminium together with about 3 to 10 per cent. of magnesium. The density of the alloy is roughly 1·7, and it is much harder, has greater strength and is more easily worked than aluminium itself. Magnalium, like aluminium, soon becomes covered with a thin film of oxide when exposed to air, and this prevents any further corrosion. The alloy is said to be similar to brass in its mechanical properties and it has been used for the framework of airships. 'Duralumin' is one of the most important of the light alloys; it contains about 4 per cent. of copper, and 0·5 per cent., or a little more, of magnesium and manganese. Its density is the same as that of aluminium. If duralumin is heated to 500° C., then quenched in water and allowed to stand, its strength increases so that it becomes equal to that of mild steel—that is several times as great as that of pure aluminium. This alloy is used for air-ship and aeroplane construction. Aluminium is also added to brass in order to harden it and increase its strength, whilst various other alloys of aluminium, copper and zinc are used for motor-car and aeroplane parts.

Some very interesting progress has been made in recent years in connexion with aluminium alloys which are not readily corroded by salt water and can, therefore, be used for marine construction. If an aluminium alloy containing from 8 to 15 per cent. of silicon is heated to about 700° with small quantities of certain salts, or oxides, or other substances, a



remarkable internal change of structure occurs. The resulting alloys possess increased strength and excellent casting properties; they are also light in weight and very resistant to corrosion. These alloys are being used for various exposed parts of ships and are apparently giving satisfaction. Since the original discovery in 1920 of the structural change which was possible in aluminium-silicon alloys attempts, many of them successful, have been made to produce similar changes in other aluminium alloys and very interesting materials are being produced. It is possible that in this way there may result a series of alloys rivalling the steels in their variation in properties but which will have the additional advantage of being light and non-corrodible. The use of aluminium has increased very greatly in recent years and may increase even further in the future, especially if the cost of the metal could be reduced. In this connexion there is a very interesting possibility which should be mentioned; all forms of clay contain a fair proportion of aluminium but so far we have discovered no simple and economical method of extracting the metal. If such a process could be devised it is not improbable that the Iron Age might yield to an Age of Light Alloys.

#### QUESTIONS

1. Which were the earliest metals to be used, and why?
2. What is the difference between cast iron, wrought iron and steel?
3. How is iron extracted from its ores?
4. Why has aluminium ceased to be the rare metal it was forty years ago?

#### SUBJECTS FOR ESSAYS AND DISCUSSION

1. The heat treatment of steel.
2. The alloys of iron.
3. The protection of iron from corrosion.
4. Aluminium: its extraction and uses.

#### FURTHER STUDY

1. The corrosion of metals.
2. The future of aluminium.
3. The chemistry of alloys.
4. The development of the iron and steel industry.

#### BOOKS TO READ

Old Trades and New Knowledge. Bragg. (Bell.)  
 Everyman's Chemistry. Hendrick. (Univ. of London Press.)  
 Creative Chemistry. Slosson. (Univ. of London Press.)  
 Chemistry in Modern Life. Arrhenius. (Chapman & Hall.)

- Chemistry in the World's Work. Howe. (Chapman & Hall.)  
Chemistry in Industry. Vol. II. (Chemical Foundation New  
York.)  
Industrial Chemistry. Vol. I. Rogers. (Constable.)

## SUGGESTIONS FOR EXPERIMENTS

- Examination of minerals.  
Physical properties of various metals and alloys.  
Corrosion of metals and alloys.  
Visit to iron foundry, steel works and blast furnace.

## CHAPTER XVIII

### NATURE AND THE LABORATORY : THE SYNTHESIS OF DYES

**I**N this and the two subsequent chapters it is proposed to give some account of the chemist's attempts to imitate the processes occurring in living organisms, and to make in the laboratory and in the factory some of the materials produced by Nature as a result of these vital processes. There are several reasons why the chemist has not been content merely to let Nature do its own work and to take the best advantage possible of the results of that work. In the first place there is the undying fire of man's curiosity to find out the 'how' and the 'why' of Nature's mysterious and wonderful work, or simply the desire for knowledge upon which the whole science of chemistry is founded. There are, however, a number of other reasons which are more likely to appeal to practical minds. Many products of plant life are useful commercially as dyestuffs, perfumes, flavouring essences or medicines, but the supply of these materials depends on the amount of land and labour which can be spared for the growth of the special plants; the steady increase of population may mean that the supply of natural products is not sufficient to meet the demand. Further, the complete failure of an important crop, as a result of attack by insects, or by disease due to bad weather conditions, is a possibility which might have serious economic consequences. In any case the growth of a plant depends on the weather, on soil conditions and on many other factors difficult to control, and consequently the plant products vary considerably from time to time and from place to place. It does not need an expert to tell us that tobacco from Virginia is different from that grown in Egypt and that both differ from the South African variety; this is possibly due to slight differences in the plant and in the soil, but there is no doubt

that climatic conditions also have some influence. A better example, perhaps, is suggested by the variations in the vintage produced at one place in different years; in these circumstances the plant and the soil remain the same but the wine made from the grapes is by no means of constant quality. The great changes experienced from year to year can be realized when the prices of different vintages are compared.

In order to overcome the difficulties and uncertainties attached to a complete reliance on natural products the chemist has intervened in some cases and been able to ease the situation; it is true that synthetic tobacco and wine have not yet been prepared, but chemistry has been a great help to the perfume industry and has saved it from almost complete failure. The method generally adopted is to obtain the desired natural product in a pure condition and to determine by analysis the chemical structure (p. 24) of its constituents. When the structure is known the chemist sets about to find a method of synthesis, that is, he finds out how to build up the product from simple substances which are readily available or which he knows how to make cheaply. By reproducing the conditions as exactly as possible not merely one chemist but any chemist in any part of the world is able, if he knows the details of the method, to synthesize an absolutely uniform and standard substance in amounts depending solely on the demand for the product and on the supply of raw materials. In this way the laboratory has come to the help of, and even triumphed over, Nature.

The substances so obtained are not to be regarded as substitutes for the natural plant products, because they are identical chemically with the latter; the main difference between them is in the method of production. It should be mentioned that in many cases we are unable, for various reasons, to prepare the desired material in the laboratory; in such instances it is often possible to discover a substitute which although quite different chemically has the same general properties. An excellent illustration of this is provided by the perfume material musk; the artificial product is quite different in its chemical structure from the natural product although its odour is so similar that it serves exactly the same purpose. This artificial musk is really a substitute for natural musk, but on the other hand artificial 'coumarin'

is identical chemically with the material obtained from the tonka-bean.

It is often asked if synthetic products are as good as natural products, but this question is not easy to answer. There is no doubt that a good synthetic or chemical indigo is just as good a dyestuff as the natural product obtained from the plant—in fact it is often better owing to its uniformity and purity; but on the other hand it is doubtful if synthetic perfumes are always as completely pleasing as the natural flower extract. There is a good reason for this: a natural perfume may be a subtle blend of a hundred or more different substances, some of which although present only in the merest traces have a great influence on the composite odour. The synthetic product will probably only contain a few of the more important constituents and so in many cases although the general sort of odour is the same the subtlety and fineness of the scent will be lacking. The growing tendency at the present time is to make use of mixtures of both natural and synthetic materials so that the desirable properties of the former, combined with the low cost of the latter, result in the production of an attractive article which is not too expensive. On the whole we shall see that the co-operation between Nature and the laboratory has been a fruitful one in very many ways.

Until a hundred years ago it was thought impossible to prepare in the laboratory any of the substances which are produced in the course of life processes; the scientists of the time considered that a special kind of force, called the 'vital force', was at work in plants and animals, and that vital products could never be produced in the absence of the living organism. In 1828, however, the German chemist Wöhler found, quite by accident, that the typical vital product urea, which is a waste material of the human and animal systems, could be made from purely inorganic or non-living sources. This discovery marked the overthrow of the vital force theory and the commencement of a new epoch in which many naturally occurring substances have been synthesized in the laboratory and on a large scale in the chemical works.

Another great step forward in synthetic chemistry was made twenty-eight years later, in 1856, also to some extent as the result of an accident. William Henry Perkin, a young London student, eighteen years of age, was engaged on what

we now know to have been a hopeless task ; he was trying to prepare the well-known drug quinine from impure aniline oil made by the chemical treatment of benzene from coal-tar. During the course of his experiments Perkin obtained a black tarry mess which most chemists of the time would have had no hesitation in throwing away ; Perkin, however, had the makings in him of a great scientist and he examined the dirty product. He found that a material which gave a purple solution could be extracted from it and that this solution could dye fabrics. Realizing the importance of this observation Perkin continued his experiments and developed a method for the manufacture of the purple dye on a large scale and in 1857 there was opened at Greenford Green, near London, the first factory for the manufacture of the synthetic dyestuff known as 'mauveine'. This was the first of the so-called 'coal-tar' or 'aniline' dyes. The dye mauveine was an entirely new one which did not exist in Nature and so the chemist was finding new scope for his investigations. Nature had made dyes in plants, and the chemist was making a dye of his own in the laboratory and in the factory.

This success stimulated the chemist in his efforts to make in the laboratory the *same* dyes as Nature made in the plant and in a short time the desired result was achieved. In 1869 Perkin, in England, and Graebe and Liebermann in Germany, devised simultaneously a method for manufacturing one of the oldest and most important of the natural dyestuffs—alizarin or Turkey red—which had up to that time only been obtained from the root of the madder plant. This dye had been produced from natural sources for thousands of years and now chemists had succeeded in making it from anthracene, one of the products of coal-tar distillation. The production of the synthetic alizarin increased very rapidly and in a few years it had completely displaced the natural product with which it was, in fact, chemically identical. Although some of the most important fundamental discoveries in connexion with this and other dyestuffs were made in England, unfortunately, for various reasons, Germany obtained almost a complete monopoly for their manufacture, and so developed the production that the synthetic dye industry became one of the most important of the country. Natural products which were more expensive and less uniform were thus not in great demand and about 50,000 acres of land in the South of

France which had been used for the cultivation of madder had to be turned to other uses ; the American writer Slosson says, in this connexion, ' French soldiers became dependent on made-in-Germany dyes for their red trousers '.

During the last sixty years over 1,000 different dye-stuffs have been made from chemical substances ; only a very few of these are found in Nature and the rest had no existence until the chemist made them. A great deal of information has been accumulated concerning the colour property associated with certain chemical groupings of elements, and so to some extent it has been possible to design a dyestuff theoretically and then to go into the laboratory and make it practically. By introducing different arrangements of atoms into the molecule it has been possible to produce different shades of colours, of varying fastness to light and varying ability to adhere to the fibre. Many of the dyes known are not satisfactory for general use: the number referred to above are commercial products. The chemist has thus made available a range of colours that could not have been imagined seventy years ago.

Most dyestuffs may, in general, be divided into three rough classes according to the method which has to be adopted to attach them to the fibre to be dyed. There are firstly the ' direct ' colours ; these may be taken up quite firmly by the clean fibre straight from the solution of the dye in some appropriate medium. The second group of dyes is known as the ' mordant ' colours which can only be attached to the fibre by means of an intermediate substance called a ' mordant '. The latter is of such a nature that it will unite very firmly with the fibre and when the resulting material is placed in a suitable dye-bath the mordant combines with the dye and forms a coloured substance which remains attached to the fibre. One of the best known mordant colours is alizarin ; using oxide of aluminium as a mordant it produces red dyes on cotton, whilst iron and chromium oxides yield purple and brown dyes respectively. The third class of dyestuffs are the ' vat ' dyes ; these, although the most expensive, are the most permanent of the colouring matters ; hence efforts are now being made to improve the production of these dyes and so lower their price. The vat dyes are not soluble in any of the liquids generally available for the dyer and so special methods have to be adopted in order to attach them to the

fibre. The dye, e.g., indigo, is generally suspended in water and a 'reducing agent' is added; the latter has the effect either of removing oxygen or adding hydrogen to the dyestuff molecule and an almost colourless substance results. This dissolves easily and from the solution it is readily taken up by the fibre; when the resulting fabric is exposed to air the oxygen reconverts the colourless substance into the original coloured dye which adheres firmly to the fibre.

It must be mentioned that since cotton, wool and silk are quite distinct from one another in their chemical nature they will behave quite differently towards a given dye-stuff; a direct cotton colour, for example, is not necessarily 'direct' either for wool or silk. As a general rule each type of fabric must be treated in its own special way. Wool and silk, however, often behave similarly to certain dyes since both these fibres are of animal origin. When a fabric consists of two or more different types of fibre then mixed dye-baths can frequently be used, or the same material is passed through two different dyes, to give the so-called 'union' fabrics in which one fibre is one colour and the other is dyed a different colour; attractive 'shot' effects are often produced in this way. The problem of dyeing artificial silk is a comparatively new one but many of the difficulties have now been overcome; the use of artificial silks of different kinds permits the production of very artistic 'union' fabrics (p. 243).

Before leaving the subject of dyes it is worth recounting the story of two of the most ancient and historical of dyestuffs, in order to illustrate some of the varied results of the friendly competition, or co-operation, between Nature and the laboratory. The most widely used, and probably the oldest of the known dye materials is indigo; wrappings of mummies discovered in the Tombs of Thebes, estimated to be about 6,000 years old, were found to be dyed with indigo. The woad with which the ancient Britons painted their bodies before entering battle was an impure form of the same dye. For thousands of years indigo was obtained from the juice of a plant and during the nineteenth century the cultivation of various species of *Indigofera* developed on a considerable scale in India. In 1895 that country produced 90 per cent. of the world's output of indigo and about a million and a half acres were under cultivation for this purpose; at the time production was at the rate



of 17 million pounds of the dyestuff per annum. Chemists, however, had already begun to turn their attention towards this important dye; in 1880 the German scientist Baeyer had succeeded in preparing indigo in his laboratory but the process was not one which could be worked economically enough to compete with the natural production of the dye. After spending over a million pounds sterling and seventeen years in experimental work a German chemical firm succeeded in 1897 in making indigo on a commercial scale. By 1900, 4½ million pounds per annum of indigo were being made synthetically and this rate grew to 80 million pounds in 1913; at that time the production of natural indigo in India had sunk to less than half a million pounds. The war of 1914 gave an impetus to the cultivation of the natural product but this has once more declined; it is estimated that at the present time the total world's output of indigo is about 100 million pounds per annum, and of this about 4 million pounds is the natural product. Indigo to-day is more uniform in quality and very much cheaper than it was thirty years ago, and hence the consumption of this dyestuff has increased six-fold; this must mean, of course, an increased demand for cloth to be dyed and on the whole an increased circulation of money. It would be interesting, if one had time, to follow out some of the economic consequences of the production of synthetic indigo in a number of different directions. Of course the Indian indigo planters have had to find some other use for their land and it appears that this has been done quite successfully.

The other story of dyestuffs is quite a different one; it concerns the famous Tyrian purple—the purple of kings. Ever since man has existed on this earth there have, no doubt, been people who have pined for the 'good old days' and deplored the degeneracy of their own times. Of this type were those who said that we had no dye to compare with the Tyrian purple of the ancients, of which Browning says 'one drop worked miracles, and coloured like Astarte's eyes'. As its name implies this dyestuff was obtained originally from the Phœnician city of Tyre; the great wealth of this town is sometimes attributed to the trade in the precious purple which was so expensive that it could only be purchased by the richest in the land. In ancient Rome to be 'born to the purple' meant that one belonged to a family of nobility

and wealth, and purple has ever since been the colour symbolic of royalty. According to Pliny the dye was obtained from a sea-snail belonging to the family known as *Murex*, and the finding of many thousands of shells of these creatures near the ruins of old dye-works at Athens and Pompeii confirms this statement. About twenty years ago the chemist Friedländer was curious to find out what the mysterious Tyrian purple really was; he procured about 12,000 *Murex* sea-snails and from these he managed to extract about a twentieth part of an ounce of the purple dye. The analysis proved a comparatively simple matter and in 1909 Friedländer announced to an interested scientific public that the main constituent of the 'purple of kings' was identical chemically with a dye that had been prepared by Sachs and Sichel in 1904, but which had no commercial value as it was inferior to many colours already on the market! Tyrian purple we now know to be a compound of bromine and indigo, united in a definite manner; a slight difference in the mode of connexion would have yielded a much better dye! It is possible, therefore, that Tyrian purple was sought after not because of its superlative beauty, but rather because it was very expensive; such is human nature!

#### QUESTIONS

1. Why does the chemist attempt to imitate Nature?
2. What was the 'vital force' theory, and how was it disproved?
3. What is Tyrian purple?
4. What is alizarin? Why is madder no longer cultivated to any extent?

#### SUBJECTS FOR ESSAYS AND DISCUSSION

1. Natural products versus synthetic products.
2. The discovery and early history of the aniline dyes.
3. The different types of dyestuffs.
4. The history of indigo.

#### FURTHER STUDY

1. The work of the dyer.
2. The history of dyestuffs.
3. Natural dyes.
4. The groups of artificial dyes.

#### BOOKS TO READ

Chemistry in the Home and Community. Beery. (Lippincott.)  
Creative Chemistry. Slosson. (Univ. of London Press.)  
Old Trades and New Knowledge. Bragg. (Bell.)

Chemical Discovery and Invention in the Twentieth Century.  
Tilden. (Routledge.)

Chemistry in Modern Life. Arrhenius. (Chapman & Hall.)

Chemistry in Industry. Vol. II. (Chemical Foundation, New  
York.)

Industrial Chemistry. Vol. II. Rogers. (Constable.)

#### SUGGESTIONS FOR EXPERIMENTS

Dyeing cotton, wool and silk with a simple water dye.

Dyeing with congo red, alizarin and indigo.

Preparation of a simple azo dye.

Visit to a dye-works.

## CHAPTER XIX

### NATURE AND THE LABORATORY: MEDICINES AND PERFUMES

**I**N the field of dye-stuffs the chemist has made his most successful attempts to imitate, and if possible improve on Nature, but in the realm of medicinal products, although his triumphs may have been less spectacular, they are probably of more profound importance. During the course of thousands of years man accumulated knowledge of a large number of naturally occurring plant products which were useful in cases of illness; this knowledge was obtained by a process of trial and error; that is by experiments on suffering human beings. Sometimes an error had unfortunate consequences; frequently the process of trial yielded no result at all, but occasionally it was successful and so useful information was slowly gathered together. Until about sixty or seventy years ago, however, the healers of the sick had at their disposal only drugs which were found in plants and these, very often, in addition to their beneficial properties also had harmful ones.

Once more the chemist has stepped in and co-operated with Nature with valuable consequences. The method adopted has generally been along the following lines. In the first place the tincture, or extract, containing the particular medicinal substance being studied is obtained from the plant; attempts are then made to identify the different substances present and to find by experiments which of these has the desired physiological—that is medicinal—effect. Once the active principle has been identified the chemist can set to work to devise methods of obtaining it in a pure condition from the plant extract on the one hand, or for making it from purely chemical sources on the other; either or both of these procedures may be adopted according to circumstances. If the natural drug has harmful properties,

which it is desired to eliminate, chemistry can often help; cocaine, for example, obtained from coca-leaves, is a very valuable local anæsthetic, but on the other hand it is extremely poisonous and liable to cause irritation when injected. Careful investigation of the way in which the complex cocaine molecule is built up from its constituent atoms has shown that at least two distinct groupings of atoms are present; one of these groups is apparently responsible for the anæsthetic properties and the other for the poisonous nature of the drug. Acting on this assumption chemists set to work to synthesize new substances having the desirable grouping of atoms but not the harmful one; they have succeeded in preparing a number of such materials, amongst which are 'beta-eucaine' and 'novocaine'. These are excellent local anæsthetics, much less poisonous than cocaine and non-irritant in their action; they are greatly used in dentistry and for other minor operations. Neither of these substances, as far as we are aware, has any existence in plant life; they are pure products of the laboratory and the imagination of the chemist, built up on the foundations laid by Nature.

It has been known for some time that an extract made from the bark of the willow, or the white poplar, was often helpful in cases of rheumatism and in fevers; investigation showed that the medicinal properties were due to a substance known as 'salicin'. Further study indicated that the active principle was really salicylic acid, which can be made synthetically from the carbolic acid of coal-tar, and this for some time replaced salicin. It was then discovered that salicylic acid was liable to cause stomach trouble and so it was modified and acetyl salicylic acid was produced; this substance is generally known as 'aspirin'. It has all the beneficial qualities of the original salicin, but is much easier and cheaper to make; like all other drugs, however, it should only be taken under medical supervision.

Not all chemical drugs have been built up as a result of information provided by Nature; sometimes the original idea was obtained by accident, as for example in the case of the drug 'phenacetin' which is used in cases of fever. In 1886 Cahn and Hepp, two medical students, were trying to find the effects of naphthalene on the human body; they found that the substance on which they were experimenting had the power of lowering the body temperature and hence

was a 'febrifuge'. It appeared later that by pure chance the material with which Cahn and Hepp were working was not naphthalene but a chemical known as acetanilide; in this way the fever reducing property of the latter was discovered accidentally. Acetanilide is somewhat poisonous on account of the aniline it produces in the body and so a chemical derivative, known as phenacetin, was prepared. This had all the desirable properties and none of the toxic ones of acetanilide, and so it is an important medicinal product at the present day.

Chloroform, as an anæsthetic, and 'chloramine T', as a powerful disinfectant, also have no counterparts or parent substances in Nature, to which they owe their origin. They are entirely the result of the joint action of chemists and physiologists. In the preparation of general anæsthetics and of narcotics, that is substances which induce sleep, the departure from Nature has probably been greater than in any other aspect of medical chemistry. At one time the only narcotics in use were made from opium, and although these were effective in inducing sleep they had very unpleasant after effects, amongst which was a craving for more of the drug; in recent years a number of synthetic narcotics have been prepared, such as 'veronal' and 'sulphonal', which are not related in any chemical way to the morphine from opium. These new narcotics can be administered in reasonable amount with perfect safety and their preparation represents one of the triumphs of chemistry.

Some of the most striking work on the application of chemistry to medicine—the science called 'chemotherapy'—was performed by the German physiologist Paul Ehrlich; the series of studies which led to the discovery of the famous drug '606' or 'salvarsan' are worth describing, although they deal with man's struggles against rather than his co-operation with Nature. It has been known for some time that simple compounds of arsenic, such as the common 'white arsenic', were useful in the treatment of certain diseases due to the presence of very simple organisms, known as 'protozoa', in the blood. These compounds of arsenic were poisonous, however, and could only be administered in small doses, and so other derivatives were sought for which would have a more powerful action yet not be toxic. In 1902 there was introduced into medicine the compound of arsenic known as

'atoxyl' which was found to be useful in combating various diseases due to protozoa, such as malaria, sleeping sickness, cattle-plague and syphilis; it had the great disadvantage, however, of endangering the eyesight and causing blindness. Whilst working on these arsenic compounds Ehrlich noted that certain dyes were absorbed by the protozoa responsible for various diseases but were without influence on the host in whose blood these parasites lived. He then conceived the idea of preparing compounds of arsenic which were similar in their structure and behaviour to these dyes; these compounds were expected, when injected into the blood of a patient, to attach themselves firmly to the protozoa and kill them but to have no influence on the tissues of the patient himself. After many unsuccessful attempts the 606th compound prepared was found to have the desired properties; it killed the protozoa but left the host unaffected and so enabled him to overcome the disease. The substance was called 'salvarsan', and various modifications of it have been used successfully in the treatment of relapsing fever, sleeping sickness, malaria and syphilis.

In recent years the German firm of Baeyer has produced a new drug called 'Baeyer 205', containing no arsenic, which is said to prevent the development of the protozoa in various tropical diseases, particularly sleeping sickness. The successful treatment of this disease is regarded as the key to Central Africa and so the actual nature of the drug is kept secret; there is very little doubt, however, that it has been developed from some dyestuff which is absorbed by the harmful organism and kills it but leaves the tissues of the host untouched.

No description of the attempts of the chemist to imitate Nature in the field of medicine would be complete without some reference to the remarkable substances known as 'hormones', or 'chemical messengers', present in the secretions which the ductless or endocrine glands of the body pour straight into the blood stream. These hormones although present only in minute amounts are apparently responsible for regulating a number of vital processes and in their absence abnormal conditions result. We have already referred to the hormone 'insulin', produced by certain parts of the pancreas, which regulates the amount of sugar in the blood (p. 131). The failure of these glands to send out insulin results in the presence of an excess of sugar and the disease

of diabetes results. An excess of insulin also leads to an abnormal condition in which there is a deficiency of blood sugar and so in the normal human being the production of the hormone must be a perfectly balanced process. Insulin has so far not been obtained in a pure condition and hence we do not know its structure ; until we know this it is quite hopeless to attempt a synthesis. It has already been stated, however (p. 133), that efforts are being made to find a chemical substitute ; these efforts have hitherto not met with any success.

As long ago as 1849 it was realized that Addison's disease was connected in some way with the supra-renal glands which are situated just above the kidneys. Further investigation showed that the normal glands produce a secretion which passes straight into the blood stream and that an extract of the glands, obtained from certain animals, could be used to some extent in treating Addison's disease. The normal supra-renal glands evidently produce a hormone ; in 1901 this was isolated in a perfectly pure condition by Takamine and called 'adrenaline'. Shortly afterwards the chemical structure was determined and the substance was first synthesized from artificial sources in 1903. At the present time the synthetic hormone is a commercial product, sometimes called 'supra-renal synthetic', and it has all the medicinal value and physiological activity of the natural extract of supra-renal glands. It is interesting to note that the injection of adrenaline into the blood produces the reactions which accompany the emotions of anger, excitement and fright ; the hair stands on end, the face becomes pale, the heart thumps, the blood pressure rises and glucose, the fuel of the body, is poured into the blood stream. A sudden fright, therefore, apparently causes the supra-renal glands to send out adrenaline into the blood stream and this hormone, or messenger, warns various parts of the body to prepare for an emergency. According to Dr. H. H. Dale, 'there is evidence that the constant presence of traces of this hormone (adrenaline) in the blood is a necessary condition for the maintenance of a healthy tone'. The chief application of adrenaline at the present time is in connexion with 'bloodless' surgery ; it has a powerful constricting action on the small blood-vessels and so drives the blood away from the point at which it is injected. A mixture of novocaine and adrenaline, therefore, has found particular favour as a local anæsthetic for small operations.



Another hormone which has been made synthetically in the laboratory is 'thyroxine', the active constituent of the secretion of the thyroid gland. This substance was first isolated in a pure condition from the glandular extracts of sheep and oxen by Kendall, in America, in 1915, but its first definite preparation from non-living sources was accomplished in this country by Barger and Harington in 1926. For a considerable time it was known that a badly developed thyroid gland, which is situated in the neck, produced a state of serious mental and physical under-development known as 'cretinism' in children, or a disease called 'myxœdema' in adults; both these abnormal conditions could be remedied by the administration of either an extract of thyroid gland or else of the dried gland itself obtained from sheep. In the absence of the thyroid secretion the body is unable to set free energy at the normal rate, and although life continues the actual metabolic rate (p. 120) may be reduced by 40 per cent. below the normal value; the addition of a suitable amount of the hormone 'thyroxine' either in the pure form, or as an extract, causes the metabolic rate to become normal. The injection of 10 milligrams—about one three-thousandth part of an ounce—into the blood of a normal individual will cause an increase of 45 per cent. in the metabolic rate and the pulse movement increases to 120 per minute; this condition is reached gradually after five days and normality is not reached for about a fortnight after the injection. The thyroid hormone, therefore, differs from that of the suprarenal gland; the former has a steady and continued action whilst the latter is chiefly useful in an emergency. If the thyroid gland functions too actively a condition of abnormality is also produced; this appears to be the cause of Graves' disease or exophthalmic goitre. It is interesting to note that thyroxine has been found to be a compound containing nearly two-thirds of its own weight of iodine, and hence small amounts of iodine are an essential constituent of human diet; as a general rule quite sufficient for the normal functioning of the body may be obtained from fruit, vegetables and milk. Sufferers from ordinary—not exophthalmic—goitre, however, are often advised to take extra iodine in other ways.

Although a number of ductless gland secretions are known, no other hormone has yet been isolated in a pure condition; the next success in this direction will probably be in connexion

with the pituitary gland, which is at the base of the brain. This gland is usually found to be enlarged in cases of 'giantism' and of abnormal growth of head, hands or feet. An extract of the gland has been made and found to have very valuable applications, especially in obstetric work, but so far no pure hormone has been obtained from it. An extremely concentrated product has been prepared, such that one part dissolved in a thousand million parts of salt solution is still physiologically active, but even this is not the pure hormone. Unfortunately only very small amounts of pituitary extract are available and so the problem of identifying the active principle and determining its structure is a matter of some difficulty.

Hormones resemble vitamins in the respect that small quantities are continually required in order that the animal organism may grow and develop normally; they both appear to be catalysts for certain life processes. There are, however, two important differences between them. In the first place the normal human being is able to make its own hormones but the vitamins must be supplied from outside, whilst in the second place an excess of hormone is just as harmful as a deficiency but an excess of vitamin has apparently no influence on the functioning of the body. Reference has already been made to the possible synthesis of vitamins in the laboratory (p. 153)

Perfumes and flavours have been extracted from various parts of plants for thousands of years; in the form of incense they were used for religious ceremonies whilst extracts were used for toilet purposes and for embalming. Most plant perfumes contain materials which have disinfectant properties and so the use of these substances, stimulated probably by vanity, played an important part in the preservation of the health of the community in days when sanitation was very primitive. The odours of flowers and various other parts of plants, we now know, are due to the presence of substances called 'essential oils', and even to-day these oils are of importance in perfumery, in medicinal work and in the preparation of flavouring essences. The essential oils are not by any means simple substances and they frequently contain a large number of different chemical compounds; some may be regarded as impurities but most of them have something definite to contribute to the odour of the oil. The odoriferous

principles are found in different parts of the plant according to its nature ; thus in the case of the carnation, hyacinth, lavender, jasmine and rose the essential oils are extracted from the flower ; with peppermint, geranium, cinnamon and verberna they come from the leaves and stem ; whilst the oils of lemon, lime and orange are obtained from the fruit.

The method of extracting the oil depends on the nature of the plant material and also on the place in which the extraction is being carried out. One of the oldest methods used is that known as 'enfleurage' ; this process depends on the fact that fats, such as lard, are able to absorb the perfume from a flower. A layer of fat is spread on a sheet of glass and fresh flowers are sprinkled on it ; when the odour of the flowers has been absorbed they are removed and a fresh quantity added. The procedure is continued until the fat has absorbed as much perfume as it will, and it is then known as 'pomade'. This may be used as such for certain toilet preparations, or else the perfume may be extracted by means of alcohol. The method is declining in popularity although it has a great deal in its favour ; it does extract the complete odour of the flower without decomposing any of the constituents of the essential oil. Unfortunately the fat is liable to become rancid and so may affect the smell of the perfume. One of the chief methods of extracting essential oils at the present day is to dissolve them out from the flowers, etc., by means of volatile solvents, such as chloroform. The oils dissolve completely in the solvent and when the latter is evaporated off under reduced pressure the pure essence is left behind ; this is regarded as one of the best modern processes. Another method often used is that of 'steam distillation' ; steam is passed through the plant material and the vapour of the oil is condensed with the steam and collected. This process of extraction never gives an essential oil with the true odour of the flower, or other material, because the different constituents do not all volatilize equally readily in the steam ; some are liable to decompose at the high temperature used, whilst others may dissolve in water and so be removed from the oil. The method of steam distillation, however, is a very convenient one and is often used. Citrus oils—from lime, lemon and orange—are of no use if steam distilled and hence the oils are extracted by squeezing the peel of the fruit.

Owing to decomposition and the difficulty of extracting

an essential oil completely it is often found that the latter does not smell quite the same as the flower from which it came ; thus oil (' attar ' or ' otto ') of roses, obtained by steam distillation, does not smell like a fresh rose. The art of perfumery, therefore, consists of mixing and blending a variety of oils and perfumes so as to get the desired effect ; the resulting product, as already mentioned, may contain a hundred or more different substances, some of them only present to a very minute extent. In the production of perfumes it is quite common to find that the addition of two or three drops of a certain substance to a gallon of essential oil has an important influence on the composite odour, and the skilled blender of perfumes knows exactly how much of each constituent is required.

In recent years the chemist has come to the aid of the perfumer and the co-operation has been very successful ; not only have methods been devised for preparing some of the plant products in the laboratory, but means have been discovered of obtaining desirable substances from useless ones. New substances which apparently do not exist in Nature but which have pleasant odours have also been made and used to mix with the plant products. Almost all the perfumes in use at the present time are a mixture of plant and synthetic products ; each contains what the other lacks. Many essential oils are extremely difficult, or else almost impossible to extract in a form in which they resemble the odour of the original flower and in such cases it is necessary to use synthetic products ; examples of such plants are the lilac, lily, hyacinth and narcissus. It is only in the cheapest perfumes, however, that entirely synthetic materials are used but as these cannot hope to reproduce exactly the odour of a flower it is quite general to use a natural oil, or a product obtained from an essential oil, as a basis.

The foundation of the commercial production of synthetic odoriferous substances was laid by Sir W. H. Perkin in 1875 when he prepared ' coumarin ' from chemical sources ; this substance is chiefly responsible for the odour of the tonka bean and the melilot. It is used at the present day as a tobacco flavour and also for confectionery and soaps ; coumarin is also the basis of the so-called ' new-mown hay ' perfume. Since this substance was synthesized many other naturally occurring materials with pleasant odours have been

obtained from coal-tar products, whilst a number of other substances have been invented. The contributions of chemistry to perfumery fall into four main divisions which will be discussed very briefly. In the first place the chemist has made use of a number of methods of obtaining useful substances from valueless ones; thus citronella oil has a disagreeable odour but from it may be extracted the very pleasant smelling substance called 'geraniol', present to a large extent in natural rose oil and other flower oils.

In the second place it has been found possible by chemical treatment to prepare desirable products from cheap raw materials. Lemon-grass oil contains an unpleasant smelling and cheap constituent called citral and this forms the raw material for the manufacture of ionone, the basis of artificial violet perfume. Natural violet oil is so expensive and difficult to extract in a satisfactory form that ionone is almost universally used at the present time; it is probably not identical with the chief constituents of violet oil, but it simulates its odour very well. Turpentine has been used as the raw material in the chemical preparation of 'terpineol', a substance found in some of the finest natural flower oils. The main odoriferous constituent of vanilla is a compound called 'vanillin' and this has been made from oil of cloves, although it is generally prepared at the present time from coal-tar products.

This leads us to the third line along which the chemist has helped the perfumer; a number of substances existing in Nature, such as coumarin and vanillin, which have already been mentioned, can be made from benzene, toluene and other raw materials obtained from non-living sources. Benzaldehyde and phenyl-ethyl-alcohol are two important substances which occur in almond oil and in rose oil respectively; they also have been synthesized and are commercial products. The latter substance is particularly useful, as attar of roses generally contains a smaller amount of it than does the flower, and hence the synthetic product can be used to adjust the odour of the oil more closely to that of the rose itself. It may be mentioned here that one of the very few essential oils to consist almost exclusively of one substance is oil of wintergreen; its main constituent is methyl salicylate which can be made from methyl alcohol (p. 178) and salicylic acid, prepared from carbolic acid. The synthetic product is almost

identical with the natural oil and is just as useful as a flavouring essence.

Finally the chemist has helped the perfumer by producing entirely new substances which do not exist in plants or animals, but which have odours resembling those of natural products. The best example of this aspect of the chemist's work is provided by the preparation of artificial musk. Musk is particularly useful in perfumery, not so much for its own odour as for its value as a binder and blender of other odoriferous substances; the natural product is obtained from the musk-deer, which is only found in the Himalayas at elevations over 8,000 feet and must be consequently very expensive. In 1888 a German, Baur, invented an artificial musk which appears to have no connexion whatever with the natural product except that it has a similar smell. This artificial musk is made from toluene—a coal-tar product—and its chemical name is tri-nitro-butyl-toluene; it is related in composition to T.N.T. (p. 114), and is in fact explosive itself. The odour of this product is not quite the same as that of natural musk but owing to its cheapness it is frequently used as a substitute. The original artificial musk has been considerably improved and the best of the new products, costing about £3 a pound against about £80 for the natural product, are used in perfumery.

The co-operation between the chemist and the perfumer has resulted in the production of an increased number of different perfumes at a cost which is distinctly lower than that of the natural materials; at the same time the odours of the new mixtures, using natural and artificial products of various kinds, frequently approach more closely those of the flowers than do the extracted essential oils. In addition, for cheap perfumes used in soaps, synthetic substances have been invented which may or may not resemble in chemical nature the natural substances they imitate. By reducing the price and improving the odours of perfumes, as well as by inventing new odours, the chemist has helped to increase very greatly the demand for scented materials. For the better scents it is an advantage to use an essential oil as a basis and so the application of chemistry to perfumes, instead of replacing the production of natural oils, has rather stimulated this industry.

## QUESTIONS

1. Outline the methods used in the discovery of synthetic drugs.
2. What is novocaine? How did it originate?
3. How were phenacetin and aspirin discovered?
4. What are 'essential' oils? How are they extracted?

## SUBJECTS FOR ESSAYS AND DISCUSSION

1. The work of Ehrlich.
2. Hormones.
3. Chemistry and medicine.
4. Chemistry and the perfume industry.

## FURTHER STUDY

1. The synthesis of hormones and their influence on life processes.
2. The perfume industry.
3. Synthetic drugs.
4. The history of drugs and perfumes.

## BOOKS TO READ

Chemistry in Industry. Vol. I. (Chemical Foundation, New York.)  
Recent Advances in Biochemistry. Pryde. (Churchill.)  
Chemistry of Commerce. Duncan. (Harper Bros.)  
Synthetic Drugs. May. (Longmans, Green.)  
Oil. Mitchell. (Pitman.)  
Books recommended for Chapter XVIII.

## SUGGESTIONS FOR EXPERIMENTS

Analysis of aspirin (acetyl salicylic acid).  
Preparation of methyl salicylate and amyl acetate.

## CHAPTER XX

### NATURE AND THE LABORATORY: ARTIFICIAL FOOD AND CLOTHING

**A** FASCINATING, as well as a difficult problem which faces the chemist, in his attempts to imitate or improve on Nature, is that of synthesizing material for food and clothing. Already it is possible to prepare in the laboratory very simple carbohydrates, or sugars, but owing to the great complexity of the various reactions involved the processes can certainly not compete with those occurring in Nature. On the other hand Professor Baly of Liverpool University and his co-workers have succeeded to some extent in imitating in the laboratory one of the processes which go on in the green plant; they exposed a solution of carbon dioxide in water to sunlight under certain conditions and obtained very minute, but quite definite, amounts of carbohydrates. Thus it may be possible to produce food material by means of the cheap method of the plant without actually using a plant! These experiments may yield very important results in the future because they not only point the way towards the production of synthetic food material but they also indicate a direction in which a larger proportion of the energy of the sun may be made available for us on the earth. At the present time plants and water power provide us with the two chief methods of using the sun's energy, and this new idea of making carbohydrates in the presence of sunlight without using a plant may give us a third method. The work is, however, still in its very preliminary stages.

Fats can also be made synthetically, but here again Nature scores on the grounds of simplicity and cheapness; in spite of this there may still be scope for the chemist. Fats are used to a great extent in the manufacture of soap (p. 85) and attempts are being made to synthesize from the hydrocarbons found in paraffin wax either fats or else fatty acids



which could be used in soap making. Stearic acid, for example, has a chain of 18 carbon atoms and hydrocarbons with equally long or longer and similar chains are found in the wax, and the conversion of the hydrocarbon into the acid is not beyond the realms of possibility ; so far, however, no successful result has been recorded. It has already been mentioned that people suffering from diabetes are unable to tolerate ordinary fats (p. 134) ; this is because common fatty acids always contain an *even* number of carbon atoms and on decomposition in the body harmful substances result which produce 'acidosis'. In 1913 Ringer suggested that fats derived from acids with an *odd* number of carbon atoms might be useful for diabetic patients but he was unable to prepare a fat of this type. Some time afterwards, however, Max Kahn in America succeeded in preparing, from stearic acid, such a substance which he called 'intarvin' ; it was said to be a true oleo-margarine product, creamy-white, odourless, tasteless, quite palatable and solid when cold. Kahn claimed that this fat could be utilized in human metabolism and did not produce acidosis in diabetics. Although these claims have not yet been definitely substantiated interesting possibilities are opened up.

The most difficult food materials to synthesize are the proteins ; these are very complex substances and so far it has only been possible to prepare some of the simpler amino-acids (p. 135), into which the proteins can be split up. No doubt a time will come when, perhaps by the aid of enzymes borrowed from natural sources, it will be possible to produce even artificial proteins.

Whilst dealing with the subject of synthetic food it would be as well to mention the substance 'saccharin', although it is not actually a food material. Saccharin was obtained by the American chemist Remsen in 1879 during the course of experiments on compounds obtained from the coal-tar product toluene. It was found to be soluble in water and to be nearly 550 times as sweet as an equal weight of cane sugar ; it is apparently quite harmless to the system and in fact passes out unchanged. For this reason saccharin, although it is an excellent sweetening agent, must not be regarded as a substitute for sugar ; the latter is a digestible food and provides the body with energy, but the former is not affected in any way. Diabetic patients, who were pre-

vented from using sugar for sweetening beverages or puddings, were compelled to use saccharin for this purpose, and although it was not a food it improved the taste of food or drink. During the last war, when the supply of sugar was greatly restricted, saccharin was used both in the army and by the general public to a considerable extent.

In reviewing the position with regard to synthetic food it appears very unlikely that natural food will ever be entirely replaced by an artificial product, although, as in the case of perfumes, there may be a close co-operation between the two possible sources. It must be remembered that food in order to be digestible must be attractive in appearance, taste and smell and also must contain the requisite type of protein, carbohydrate and fat; possibly the chemist will supply the three essential ingredients while Nature will be called on to supply the three qualities mentioned. Natural food from plant sources can not only be made attractive but it is also of low cost as the plant works very cheaply; by a careful study of fertilizers it will, no doubt, be possible to make the plant work even more efficiently in the future. Vegetable life also provides us with a means of regulating the amount of carbon dioxide in the air (p. 103) and until the chemist discovers a simple method for converting on a large scale carbon dioxide into oxygen, as the green plant does in sunlight, vegetable life must be continued. The most probable line of development in connexion with food is, as already indicated, a co-operation between Nature and the laboratory.

The production of artificial fibres for clothing material is by no means a simple problem and here again Nature is likely to lead the way for many hundreds of years on the score of economy. The only appreciable progress which has been made in this direction hitherto is in connexion with the production of artificial silk, or 'rayon'. As a matter of fact artificial silk is neither artificial nor is it silk! Since it is always made from the naturally occurring materials wood and cotton it can hardly be described as artificial in the first place, whilst in the second place most of the so-called artificial silk is identical chemically with cotton—that is, it is a form of cellulose—whilst real silk consists mainly of protein substances containing nitrogen. In the course of making its cocoon the silkworm emits from each of two very fine orifices in its head a continuous stream of a protein body known as

'fibroin'; as they pass out these streams are hardened into fine fibres and they are surrounded and cemented together by a gummy material called 'sericin'. In the course of the preparation of silk thread from the cocoon the gum is removed and there remains a pair of long, fine and smooth fibres which have, when spun, a characteristic lustre and feel.

For about 200 years the possibility of making imitation silk from long, even fibres of material made in the laboratory had been considered, but the first successful attempt was made by Count Hilaire de Chardonnet, a Frenchman, in 1884. Whilst a student of the Polytechnic School in Paris he conceived the idea of forcing a solution of collodion, which is nitro-cellulose (p. 114) dissolved in a mixture of alcohol and ether, through a very fine jet. As the liquid was emitted the alcohol and ether evaporated off very rapidly and left behind an extremely fine and continuous fibre; by spinning a number of such fibres together a glossy silk-like thread was obtained. Samples of this imitation nitro-cellulose silk were shown at the Paris Exhibition of 1889 and two years later a factory was started for the manufacture of 'Chardonnet silk' on a large scale. Unfortunately nitro-cellulose is a very inflammable material and hence the new silk could not be used with any degree of safety until a method was discovered for removing the dangerous 'nitro' groups from the nitro-cellulose molecule. This was eventually accomplished by means of a solution of sodium, or ammonium, sulphide and the resulting product still maintained its silk-like appearance but was non-inflammable. The Chardonnet process for making artificial silk is still used by the Tubize Company in Belgium but its use in Great Britain has been discontinued owing to the high cost of the raw materials.

In 1892 Cross, Bevan and Beadle of this country patented a new method for producing fine, glossy fibres which could be used in making artificial silk; this is known as the Viscose process and it is not only the most important one in Great Britain, but it is responsible for about four-fifths of the total world production of the material. In this process, which is chiefly worked by Courtaulds Ltd. in this country and the associated Viscose Company in America, pulp obtained from wood, generally spruce, or from purified cotton is first immersed in a solution of caustic soda and then carbon disulphide is added; the cellulose of the pulp is converted into a compound,

known as a 'xanthate', soluble in water. This solution is then allowed to stand for some time so as to 'mature' and the resulting 'viscose' is forced through very fine jets into an acid bath which causes the thin stream of liquid to set into a continuous and even fibre consisting of cellulose. The fibres are then washed to remove chemical impurities, dried and spun into threads. As a result of much experimental work the process has been so improved in recent years that a strong and beautiful material can be produced at low cost.

'Cuprammonium silk' is also manufactured to some extent in this country, chiefly by the Brysilka Company; this type of artificial silk is more expensive than the viscose material, but it is said to be more like real silk in appearance and in smoothness to the touch. The original suggestion for the process used in its production was made by Despeissis, of Switzerland, in 1890, but he, unfortunately, died before the method could be tried on a commercial scale. A few years later the idea was developed by various scientists and the process is now used mainly by the Glanzstoff Company in Germany. Cotton is purified and immersed in caustic soda solution; it is then dissolved in a solution of copper oxide in ammonia. The resulting liquid is forced through fine jets, as in the other processes, into a coagulating bath containing dilute acid and various salts. The resulting fibre of cellulose is washed, dried and spun into thread in the ordinary way.

It should be noted that in the three processes already described for the manufacture of artificial silk the final product is really a form of cellulose in each case; instead of the fibres being short and uneven, as they are in the original cotton or wood pulp, they have been regenerated in a fine, smooth and continuous form with a high lustre. Chemically the artificial silk and cotton are almost identical but they differ in their physical appearance. There is, however, another form of artificial silk which differs chemically from cotton although it starts with cellulose as its raw material; this substance is known as cellulose acetate and appears on the market chiefly as Celanese which is manufactured in this country. The first patents for the manufacture of cellulose acetate were taken out by Cross in 1894 and the process was improved by Miles, in America, in 1905. The methods in use at the present day are based on the Miles patents although a vast amount of research has resulted in a great many im-

provements. Wood pulp, or bleached cotton is treated with strong acetic acid and acetic anhydride—which may be regarded as an extra concentrated form of acetic acid—together with a little sulphuric acid. The cellulose dissolves and on pouring the mixture into water cellulose acetate is thrown down in the form of white flocks; these are filtered off, washed, dried and dissolved in acetone. The resulting viscous solution is forced through fine orifices into hot air; the latter causes the acetone to evaporate and leaves thin threads of cellulose acetate which can be spun together to produce a glossy almost non-inflammable fibre. Other forms of cellulose acetate are used in the preparation of non-inflammable cinema films, for insulating materials, in the production of artificial bristles and hair, for imitation horn and tortoise-shell, and for unbreakable 'glass'.

In comparing real silk with artificial silk it is found that the former is stronger, especially when moist; in fact, one of the great disadvantages of the 'artificial' fibre is its great weakness when in a wet condition. Cellulose acetate silk is apparently the fabric which most resembles ordinary silk in its strength when damp, but even this is not as good as the natural material. Artificial silk is if anything too lustrous, and efforts have been made recently to tone this down and to increase the softness of the fibre so that it resembles more closely real silk. This has been accomplished to some extent by decreasing the thickness of the individual filaments and spinning more together in each fibre; on the average 1 pound of artificial silk now consists of 1,200 miles of filament. Since artificial silk is a fairly good conductor of heat it feels cold to the touch, and garments made of this material do not maintain the warmth of the body nearly as well as those of real silk. At the present time there is a marked tendency towards the production of union fabrics consisting of artificial silk and cotton, or wool, or real silk; in the first case we get increased strength when moist, in the second increased warmth and decreased gloss, and in the third improved softness. Each type of fibre has its own advantages, and very useful materials, which are finding increasing application in the preparation of various articles of clothing, and for decorative purposes, are being made in increasing amounts.

The dyeing of artificial silk of the regenerated cellulose type, namely Chardonnet, Viscose and Cuprammonium silks,

is a comparatively simple matter ; they take the same dyes as cotton with which they are, as already mentioned, chemically almost identical. Cellulose acetate, however, presents special problems ; none of the ordinary dyes will affect this fabric and in fact until about ten years ago it was regarded as almost impossible to dye. A group of colours called Ionamines were discovered which could dye acetate silk, but these have been displaced to a great extent by the invention of a new method of dyeing, so that it is now possible to dye Celanese almost any desired shade of colour. The difference in the reaction to dyes shown by the two kinds of artificial silk and by other fibres has made the union fabrics, mentioned above, even more valuable. By dipping such fabrics into baths containing a mixture of certain dyes various cross dyeing effects of great beauty may be obtained, and so the union materials can be made extremely attractive in appearance.

The low price, attractive nature, and good wearing qualities of artificial silk in the dry state have resulted in a very great demand for this material. In 1891 when the first imitation silk was manufactured commercially the world's output was 30,000 pounds, but this had increased to 2 million pounds in 1898 whilst in 1927 at least 250 million pounds of artificial silk were produced ; of this total 39 million pounds were made in Great Britain and about 75 million pounds in the U.S.A. Up to the present artificial silk has not replaced real silk to any appreciable extent since each has had its own sphere of usefulness, but improvements in the artificial fibre may in time cause it to be a serious competitor.

In reviewing the wonderful progress made by chemistry during the past 2,000 years two important points stand out most clearly. In the first place it will be realized that purely scientific investigations often have far-reaching economic consequences, and in this connexion we may say that Robert Boyle, by indicating the importance of fundamental chemical study—the search for truth—really showed the way to the discovery of the philosopher's stone which could turn waste materials into precious ones. On the other hand, although the work of the alchemists who preceded Boyle was of a mystical and obscure nature yet we must realize that the chemistry of to-day has risen phoenix-like

from the dead ashes of alchemy. During the seventeenth century Francis Bacon wrote 'Alchemy may be compared to the man who has told his sons that he has left them gold buried somewhere in his vineyard; where they by digging found no gold, but by turning up the roots of the vine procured a plentiful vintage'. In the course of this book some attempt has been made to describe the romantic and stimulating wine this vintage has produced.

#### QUESTIONS

1. Are synthetic food and clothing (a) probable, (b) desirable?
2. What is 'intarvin'? What is supposed to be its function?
3. What is artificial silk? Why is it considered to be misnamed?
4. How are artificial silks dyed?

#### SUBJECTS FOR ESSAYS AND DISCUSSION

1. The advantages and disadvantages of synthetic food.
2. The manufacture of artificial silk.
3. The economic importance of the artificial silk industry.
4. The advantages and disadvantages of artificial silk.

#### FURTHER STUDY

1. The synthesis of carbohydrates.
2. The uses of cellulose and cellulose products.
3. The history of the artificial silk industry and its probable developments.
4. Chemistry and industrial progress.

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Old Trades and New Knowledge. Bragg. (Bell.)  
Chemistry in Industry. Vol. II. (Chemical Foundation, New York.)  
Chemistry in the Home and Community. Beery. (Lippincott.)  
Creative Chemistry. Slosson. (Univ. of London Press.)  
Industrial Chemistry. Vol. II. Rogers. (Constable.)

#### SUGGESTIONS FOR EXPERIMENTS

Dyeing of various types of artificial silks.  
Testing strength of various fabrics when wet.  
Examination of union fabrics.

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